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*(1st Edition)*

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# THE DETECTION AND IDENTIFICATION OF WAR GASES

## CHAPTER I.—THE WAR GASES: INTRODUCTORY.

### (1) *General Considerations.*

The term "Gas," when used in connection with chemical warfare, includes any chemical substance, whether solid, liquid, or gas, which is employed in war for its poisonous or irritant effects on the human body.

Theoretically, all substances having such effects could be used as war gases, but in practice a number of other considerations enter. In addition to possessing adequate and utilisable physiological action there is, for example, the question of production—the substance must be relatively cheap and capable of practical and economical production from available raw materials. Again, it must have suitable physical and chemical properties—its vapour pressure, for example, must be sufficiently high to give effective concentrations under ordinary conditions, and it must be comparatively stable and chemically indifferent so as not to be too rapidly destroyed by atmospheric or other agents.

These considerations limit the choice enormously. It has been estimated that during the Great War some three to four thousand substances were examined as to their suitability for use as war gases. Of these, however, only about 54 were ever actually used in the field: and of these again, only 12 were in active use at the end of the war. A few substances have since been suggested as possibilities, but the number still remains reasonably small.

### (2) *Classification.*

The war gases differ considerably in physical properties and chemical nature, and the only reasonably satisfactory way of classifying them is according to the effects which they produce on the human body. On this basis the gases are divided into four groups according to whether their predominant action is on the lungs, the eyes, the nose, or the skin.

*The Lung Irritants*, also known as Choking gases or Asphyxiants (Suffocants), function by their action on the respiratory system, and are highly lethal. They irritate the throat and lungs, causing coughing and difficulty in breathing, and in severe cases give rise to acute pulmonary oedema. The most important members of this group are chlorine, phosgene, diphosgene and chloropicrin.

*The Eye Irritants*, more commonly known as Tear gases or Lachrymators, act, as their name implies, on the eyes, causing intense smarting and a profuse flow of tears, but without normally effecting any permanent damage. The members of this



group are, for the most part, aromatic halides, halogenated ketones, or halogenated esters, typical examples being xylyl bromide (German T-Stoff), bromacetone (German B-Stoff), ethyl iodoacetate (K.S.K.), and the more recent bromobenzyl cyanide (B.B.C.), and chloracetophenone (C.A.P.).

*The Nose Irritants*, also known as Sternutators or Sneezing gases, give rise to intense pain in the nose, throat and chest, accompanied by nausea and mental depression. As with the tear gases, the effect is only temporary, though the symptoms develop slowly and may continue for some hours after exposure to the gas. The members of this group are aromatic arsenical derivatives, known for simplicity by their code letters, D.A., D.C., and D.M.

*The Skin Irritants*, also termed Blister gases or Vesicants, exert an aggressive action on all parts of the body with which they come into contact—eyes, lungs, skin, etc.—whether as vapour or liquid, causing intense irritation, and in severe cases deep and extensive blistering. Their effect, moreover, is more or less delayed—a circumstance which makes them doubly dangerous; no immediate irritation is felt, the symptoms only developing some time after exposure, when it is too late to take protective measures. To this group belong the well-known mustard gas and lewisite.

This classification, incidentally, corresponds in essentials to that used by the Germans, who refer to the groups as Green Cross, White Cross, Blue Cross, and Yellow Cross respectively, in allusion to the markings used by them on shell. As with most classifications a certain amount of overlapping occurs; chloropicrin, for example, is quite an efficient lachrymator: lewisite is markedly irritant to the nose and throat: and chloracetophenone in strong concentrations has a definite, though temporary, irritant action on the skin. There are also one or two gases which cannot be satisfactorily fitted into the scheme, such as the infrequently used hydrocyanic acid and hydrogen sulphide, which are usually placed in a fifth group of *Paralysants*, since they function by paralysing the central nervous system. From the practical aspect, however, the classification is of definite value, in that it stresses the purpose for which the different gases are used, and the dangers to be apprehended from their use.

### (3) *General Properties.*

Before outlining the characteristics of the individual war gases, it will be convenient to deal generally with their properties as a class, and in so doing to draw attention to a further, and very important, way of grouping them—namely, classification according to persistence, which depends primarily on considerations of vapour pressure.



(a) *Vapour pressure, Volatility, and Persistence.*—Vapour pressure, which is, of course, closely allied with boiling point, is of particular importance in two directions. In the first place it determines the so-called “Volatility,” or Saturation concentration of the gas, i.e., the maximum concentration of vapour which it is possible to obtain under given climatic conditions: and in the second place, it governs the “Persistence” of the gas, which may be roughly defined as the time during which it remains effective at the point of release.

The *Volatility*, which may be expressed as weight (mgms.) of substance which saturates 1 cubic metre of air at the temperature under consideration (or alternatively as parts per million), is obtained by calculation as follows:—

If the vapour pressure of the substance is  $p$  mm. Hg. at a given temperature  $t^{\circ}\text{C.}$ , then  $\frac{p}{760}$  c.c. of vapour saturate 1 c.c. of air, and  $\frac{10^6 p}{760}$  c.c. of vapour saturate 1 cu.m. of air (=parts per million). Or, since the vapour density of the substance, assuming it to be a perfect gas, is  $\frac{M}{22.4} \times \frac{273}{(273+t)}$  gms./litre, or mgms./c.c., the saturation concentration is  $\frac{10^6 p}{760} \times \frac{M}{22.4} \times \frac{273}{(273+t)}$  mgms./cu.m., ( $M$  being the molecular weight).

The Volatility is, naturally, of considerable importance in connection with liquids used as lethal war gases, since it is obviously essential that the concentrations obtainable under ordinary conditions should be sufficiently high to be rapidly effective.

As regards *Persistence*, many factors enter, but the most important is the rate of evaporation of the liquid gas, which depends primarily on its vapour pressure—the lower the vapour pressure, the slower the rate of evaporation and the greater the persistence. Making certain assumptions it is possible to estimate the rate of evaporation, and inversely the persistence, of a liquid as compared with that of water under similar conditions, the values so obtained for some of the war gases being given in Table I.

The figures, it should be noted, are essentially relative and have no absolute significance. The actual persistence will depend, *inter alia*, on the weather and the nature of the ground and surface. High temperatures and wind velocities, for example, will favour rapid evaporation: rain will effect a certain amount of mechanical washing away and in some cases destruction by hydrolysis: the persistence will be considerably greater in sheltered terrain than in the open, and similarly will be less if the liquid falls on impervious rocky material on which it spreads without sinking in, than if it falls on a porous material such as sand, where the reverse process will occur.

The chief merit of the figures is to illustrate the fundamental distinction between the non-persistent and the persistent gases.



The *non-persistent* gases vaporise rapidly when released to form a very concentrated and hence highly toxic cloud, which, however, drifts away with the wind and becomes more or less speedily diluted with the atmosphere. On the other hand, the *persistent* gases, when released, contaminate the surrounding ground, etc., with relatively high-boiling liquid which evaporates slowly and continues to give off dangerous vapour for a comparatively long time, making it necessary to apply some form of "decontamination" treatment to render it innocuous.

This distinction has an important bearing on the way in which the different gases are used in warfare. Both non-persistent and persistent gases can be used in shell and bombs, but for more or less obvious reasons, only the really non-persistent type can be released as clouds from cylinders, and only the persistent as spray from aircraft.

It also has an important bearing on the work of the Gas Identification Officer. With non-persistent gases, if he is on the spot when the gas is released, a very high concentration will be encountered. Normally, however, the gas will be dispersed to a greater or lesser extent by the time he arrives on the scene, and in the case of the very non-persistent gases such as chlorine and phosgene it will, naturally, be relatively useless to look for samples of materials contaminated with the liquid gas. With persistent gases, on the other hand, owing to their lower vapour pressure, the concentration in the air is never very high, but evidence of ground contamination will almost invariably be found for hours or even days afterwards.

(b) *Vapour Density* also affects the persistence to some extent, gases lighter than air being more readily dispersed by diffusion, etc., than the heavier ones, which tend to cling to the ground and follow downward currents. All the important war gases have vapour densities considerably greater than that of air, ranging from 2.5 in the case of chlorine to 7.4 with K.S.K. (v. Table I). Relative lightness was, incidentally, one of the chief reasons why hydrocyanic acid (relative vapour density 0.94) did not prove satisfactory as a war gas.

(c) *Freezing Point* is not, in general, a very important factor, most of the war gases remaining liquid down to temperatures well below those likely to be met with under normal conditions. Mustard gas, however, has a relatively high freezing point ( $14.4^{\circ}\text{C.}$ ) and if used in a pure form on a cold day would probably freeze in the weapon with possible introduction of difficulties in connection with ballistics and dispersion. In practice, therefore, mustard gas is generally mixed with some 15-20 per cent. of diluent such as carbon tetrachloride or chlorobenzene, to depress its freezing point to below  $5^{\circ}\text{C.}$ , and so preclude freezing under normal conditions. Certain other gases, e.g., B.B.C. (F.P.  $25.5^{\circ}\text{C.}$ ) have to be similarly treated.



In connection with freezing point, also, reference must be made to the war "gases" which are really solids, such as C.A.P. (M.P.  $58^{\circ}$  C.), and the arsenical nose irritants (M.P. ranging from ca.  $32$  to  $195^{\circ}$  C.). The latter substances, in particular, have very low vapour pressures and would be useless as war gases except for the circumstance that they can be dispersed by heat, etc., in the form of a "smoke" or particulate cloud, consisting of very small particles (ca.  $10^{-4}$  to  $10^{-5}$  mm. diameter) suspended in the atmosphere, and in this condition capable of exerting an irritant action on the nose and throat. So, too, with C.A.P., though in the case of this substance the vapour itself is also capable of causing irritant effects.

Such particulate clouds are classed as non-persistent since they are rapidly dissipated by wind as are the true non-persistent gases. Special types of bombs and thermogenerators similar in principle to smoke candles have been developed for their employment in warfare. They were originally introduced as "mask breakers"—the particles not being absorbed by active charcoal as are vapours, but necessitating the use of special filters—and this aspect is of importance in connection with their detection: they cannot be satisfactorily sampled by the usual technique of absorption in solvents, but require a suitable filter. At the same time, they are effective in exceedingly low concentrations and are non-persistent, so that the prospect of obtaining an analysable sample is usually remote.

(d) *The Specific Gravity* in the liquid state of the gases used during the war exhibited considerable divergence, though it was appreciated that for use as shell chargings the specific gravity should approximate to that of the explosive charge which they replaced (ca. 1.5) so as not to introduce ballistic difficulties. All the more important war gases when in the liquid state have a density greater than unity, and will therefore sink if dropped into water (v. Table I).

(e) *Stability*. As regards the chemical properties of the war gases, their behaviour towards water is perhaps of greatest importance, particularly in connection with their persistence under wet climatic conditions. Most of the gases are relatively insoluble in water: some, such as chloropicrin, are practically unaffected by it: others, like mustard gas, are slowly hydrolysed: while still others, for example, phosgene and lewisite, are rapidly decomposed. Evidently, therefore, in rainy weather the latter will be relatively ineffective, and the persistence of mustard gas will be considerably reduced, quite apart from any mechanical washing away that may occur.

From the point of view of method of use, the stability of the gases to heat and explosion, and their action on metals, are also of considerable importance. The behaviour of the gases to so-called neutralising agents, such as alkalis and oxidising



agents, is similarly of importance from the defensive aspect. These and similar matters are, however, best considered under the individual war gases.

#### (4) *Physiological Effects.*

The physiological effects of the different war gases, briefly referred to in Section (2) above, are fully described in A.R.P. Handbooks Nos. 2 and 3, which should be read in conjunction with these notes (*cf.* also Table II).

From the point of view of detection and identification, physiological effect may afford a valuable warning indication of the presence of those war gases which exert an immediate irritant action on some part of the body, and this aspect is dealt with in Section (12) (d) below.

## CHAPTER II: THE WAR GASES; PHYSICAL AND CHEMICAL PROPERTIES.

#### (5) *Lung Irritants.*

Under ordinary conditions the members of this group are either true gases or volatile, low-boiling liquids. They form highly concentrated, non-persistent clouds on release, and possess, in general, a characteristic irritant odour. Most of the war-time lung irritants were, to quote Prof. Izzard, used "with no other object than to realize a provisional solution", and their future employment is improbable. Those described below were the only ones used extensively throughout the war, and with the possible exception of chlorine, which is now largely of historical interest, are probably destined to play an important rôle in gas-warfare of the future.

(a) *Chlorine* ( $\text{Cl}_2$ ) has the doubtful honour of being the only elementary substance, and the first lethal gas, to be used on an effective scale during the war, being first employed by the Germans on April 22nd, 1915, when 168 tons were released on a 4-mile front against British and French Colonial troops at Ypres, causing some 15,000 casualties, a third of which were fatal.

It is, as is well known, a gas of yellowish-green colour, which is readily liquefiable to a yellow liquid boiling at  $-33.6^\circ\text{C}$ . The gas is approximately 2.5 times as heavy as air, and is soluble in half its own volume of water. It is also soluble in a number of chlorinated hydrocarbons (*e.g.* carbon tetrachloride, tetrachlorethane, etc.).

It is very reactive chemically, acting as a powerful oxidizing agent. It vigorously attacks metals, especially in the presence of moisture; but liquid chlorine, if dry, has no action on steel, whence the possibility of storing it in cylinders, etc.



(b) *Phosgene* (C.G.) (Carbonyl chloride:  $\text{COCl}_2$ ). Phosgene was extensively employed in industry in pre-war days without any great anxiety about its toxic properties. It was first used in war by the Germans in December 1915, and remained throughout the war the principal lethal gas.

Under ordinary conditions it is a colourless, non-persistent gas, having a characteristic odour variously described as resembling that of musty hay, putrefying fruit, decaying leaves, etc. It condenses on cooling to a mobile liquid, B.P.  $8.2^\circ\text{C}$ . and D. 1.42, which is colourless if pure, though the technical product is usually yellow.

It is very readily soluble in organic solvents, in fats and oils and in various inorganic halides such as arsenious chloride, stannic chloride, sulphur monochloride, etc. It is soluble in its own volume of water, but is rapidly hydrolysed to carbon dioxide and hydrochloric acid, especially in the presence of alkali.

Like all chloranhydrides it is a very reactive substance, the chlorine atoms being readily replaced by reaction with alcohols, phenols, amines, etc. Reactions of this type were, it may be recalled, originally used for protection against phosgene, the old type PH gas helmet being impregnated with sodium phenate and hexamine. It does not attack metals if dry—whence its use in metal containers—but is very corrosive in the presence of moisture, especially to copper alloys.

(c) *Diphosgene* (Trichloromethyl chloroformate:  $\text{Cl.COOCCl}_3$ ), known to the French as Surpalite, and to the Germans as Perstoff, was one of the principal lethal gases used by them in shell during the war.

Diphosgene, when pure, is a colourless, mobile liquid having D. 1.65 and B.P.  $128^\circ\text{C}$ . Its vapour pressure at  $20^\circ\text{C}$ . is 10.3 mm., so that although considerably more persistent than chlorine or phosgene, it is still volatile enough to be classed as non-persistent. The vapour has an odour resembling that of phosgene, but somewhat more pungent.

It derives its name, diphosgene, from the circumstance that it is decomposed into two molecules of phosgene by heat, detonation, etc., and further, reacts with water and amines as if consisting of two molecules of phosgene. It is corrosive to metals when moist, but does not attack steel if dry.

(d) *Chloropicrin* (P.S.) (Trichloronitromethane:  $\text{CCl}_3.\text{NO}_2$ ), known as Klop to the Germans, as Aquinite to the French, and sometimes as Vomiting gas to the British, was first used by the Russians in 1916, and was later extensively employed by the Allies as a constituent of their penetrating NC. mixture (80 per cent. chloropicrin plus 20 per cent. stannic chloride).



When pure it is a colourless, oily, and refractive liquid of D. 1.66 and B.P. 112°C., the technical product being usually yellow. Its vapour pressure at 20°C. is 18.3 mm., so that like diphosgene it is relatively non-persistent, though not so readily dispersed as chlorine and phosgene. The vapour has a characteristic sweetish smell and pronounced lachrymatory properties.

Chloropicrin is comparatively insoluble in water (*ca.* 0.17 per cent. at ordinary temperature) but soluble in organic solvents. It is a stable compound, not hydrolysed by water, and unaffected by ordinary acids and alkalis; it is, however, slowly decomposed in the cold by alcoholic soda, and by an aqueous-alcoholic solution of sodium sulphite. It is also decomposed by alkali polysulphides.

It is partially dissociated on heating into nitrosyl chloride and phosgene, and is liable to explode on rapid heating. It has a marked corrosive action on metals when wet, but the action is superficial only, and the liquid can therefore be used in metal containers.

#### (6) *Lachrymators.*

The lachrymatory war gases are, for the most part, heavy, oily, and relatively high-boiling liquids, which in the crude state are dark-coloured owing to decomposition. They are mostly insoluble in water, but hydrolysed to a greater or lesser extent by alkalis (especially in alcohol), and are very corrosive to metals. Their vapours, which are colourless and strongly lachrymatory, possess, in general, a characteristic pungent, but not unpleasant, odour.

By reason of their relatively inferior lachrymatory properties it is doubtful whether the majority of the war-time lachrymators will be extensively used in future. As, however, several of them are still employed in various countries for training purposes, a brief description of their salient characteristics is given below.

(a) *Xylyl bromide* (German T-Stoff) ( $\text{CH}_3\text{.C}_6\text{H}_4\text{.CH}_2\text{Br}$ ). A crude mixture of *o*-, *m*-, and *p*-xylyl bromides, obtained by direct bromination of xylene, and hence usually containing the corresponding xylylene bromides  $\text{C}_6\text{H}_4(\text{CH}_2\text{Br})_2$  also, was much used as a lachrymatory shell-filling by the Germans during the war.

The mixture is a black liquid of D 1.4 and B.P. 210-220°C., which corrodes iron and steel rapidly. It is persistent (vapour pressure *ca.* 0.07 mm. at 20°C.), and its heavy vapours have a pungent aromatic odour which, in dilution, resembles that of Lilacs or Elder-leaves—whence the British war-time name, Elder-gas. It is insoluble in water, but is readily hydrolysed by alkali, and converted by energetic oxidation into a mixture of phthalic acids.



*Benzyl bromide* ( $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ , B.P.  $200^\circ\text{C}$ ., D. 1.44), the French Cyclite, is very similar in properties to xylyl bromide, but its vapours are less lachrymatory, and possess an aromatic odour resembling that of water-cress.

(b) *Bromacetone* (B.A.) ( $\text{CH}_3\text{COCH}_2\text{Br}$ ), obtained by bromination of acetone, was used by the Germans as B-Stoff, and by the French, in 80/20 admixture with chloracetone, as Martonite.

When pure it is a colourless, insoluble oil of D 1.6 and B.P.  $136^\circ\text{C}$ ., which is very corrosive to iron, and tends to resinify on exposure to light. It is a relatively volatile substance (vapour pressure 9 mm. at  $20^\circ\text{C}$ .), and toxic concentrations of its pungent lachrymatory vapours may be encountered in the field. The liquid, in contact with skin, produces painful blisters which, however, heal quickly. It exhibits all the characteristic reactions of ketones, and the halogen atom is readily removed by treatment with sodium thiosulphate or alkali.

The *bromo-methyl ethyl ketones* ( $\text{Et.CO.CH}_2\text{Br}$ , B.P.  $145^\circ\text{C}$ ., and  $\text{Me.CO.CHBr.Me}$ , B.P.  $133^\circ\text{C}$ .) possess analogous properties, but are less lachrymatory than bromacetone. They were introduced as war gases (Bn-Stoff) by the Germans when the shortage of acetone began to be felt.

(c) *Ethyl Iodoacetate* (K.S.K.) ( $\text{CH}_2\text{I.CO.OEt}$ ) was used solely by the British, and was developed on account of the shortage of bromine. When pure it is a colourless, heavy oil of B.P.  $179^\circ\text{C}$ . It slowly decomposes, however, especially in light, with liberation of iodine, and the technical product is usually dark brown-violet in colour.

It is a relatively persistent substance, its vapour pressure at  $20^\circ\text{C}$ . being 0.54 mm. The vapour has a "pear-drop" odour, and a density (air = 1) of 7.4. It is insoluble in, and stable to, water, and is only slowly hydrolysed by hot aqueous alkali. It reacts, however, with alcoholic alkali and with sodium thiosulphate solution, and is decomposed by conc. nitric acid. It was generally used admixed with alcohol or ethyl acetate. Like the majority of liquid lachrymators it corrodes metals.

*Ethyl bromacetate* ( $\text{CH}_2\text{Br.CO.OEt}$ , B.P.  $169^\circ\text{C}$ .) resembles K.S.K. in its general properties, but is considerably less effective as a lachrymator.

(d) *Bromobenzyl cyanide* (B.B.C. ; American C.A.) ( $\text{Ph.CHBr.CN}$ ), or more correctly phenyl bromacetonitrile, was experimentally tried out towards the end of the war, but is mostly a post-war development, much favoured by the French and Americans under the name Camite.



When pure it consists of yellowish crystals of M.P.  $25.5^{\circ}\text{C}$ . which slowly turn red by decomposition. The technical product, which usually contains unbrominated benzyl cyanide, is an oily brown liquid with a penetrating, but not unpleasant, bitter-sweet odour resembling that of sour fruit. The liquid has  $D_{20} 1.52$ , and boils at  $242^{\circ}\text{C}$ . with decomposition ( $133^{\circ}\text{C}/12\text{ mm.}$ ). Its vapour pressure at  $20^{\circ}\text{C}$ . is very low ( $0.012\text{ mm.}$ ), and the liquid is, accordingly, very persistent.

It is insoluble in, and unaffected by water, but soluble in organic solvents. Chemically it is a stable substance, being only slowly hydrolysed by hot aqueous alkalis, and attacked by strong oxidising agents. It is, however, hydrolysed in the cold by alcoholic alkali. Its great disadvantages from the chemical warfare aspect are that it attacks metals (except lead), losing its lachrymatory properties, thus necessitating the use of specially constructed lined containers, and that it is decomposed by heat and is sensitive to detonation.

(e) *Chloracetophenone* (C.A.P.: American C.N.) ( $\text{Ph.CO.CH}_2\text{Cl}$ ). Although first prepared in 1871, this substance is an entirely post-war chemical warfare development, and stands in rather a different category from the other lachrymators. It is a white crystalline solid, melting at  $58^{\circ}\text{C}$ ., the vapour of which has a pleasant aromatic odour resembling that of apple-blossom. As a chemical warfare agent it is dispersed by heat in the form of a non-persistent particulate cloud.

It is practically insoluble in water (*ca.* 0.1 per cent. at ordinary temperature), but soluble in most organic solvents. It is a stable compound, unaffected by boiling water, but the chlorine is readily removed by hydrolysis with alkali. Its great advantages over other lachrymators are that it does not attack iron, and is insensitive to heat and detonation.

#### (7) *Nose Irritants.*

The nose irritant gases were introduced by the Germans, simultaneously with vesicants, in an attempt to overcome the condition of "stalemate" into which chemical warfare had lapsed by the summer of 1917. They were, as mentioned above, intended as "mask-breakers", but were not, as a matter of fact, very successful in this respect, chiefly because the method of use (employment in modified H.E. shell) did not give a good particulate cloud. Under ordinary conditions they are crystalline solids with negligible vapour pressures. Chemically they are aromatic arsenical derivatives, practically insoluble in water, but readily hydrolysed by alkalis, and oxidised by oxidising agents.



(a) *Diphenyl chlorarsine* (D.A.) ( $\text{Ph}_2\text{AsCl}$ ). German "Clark I". When pure it forms white crystals of M.P.  $38\text{--}9^\circ\text{C}$ . (a labile modification of M.P.  $18\cdot2^\circ\text{C}$ . also exists), but the technical product is usually a brownish-white semi-solid mass. It is soluble to some extent in the usual organic solvents, but is only slightly soluble in water (*ca.* 0·2 per cent.), by which it is slowly hydrolysed, the hydrolysis being rapid in the presence of alkali. It is not decomposed by heat or detonation, and does not corrode iron and steel.

(b) *Diphenyl cyanarsine* (D.C.) ( $\text{Ph}_2\text{AsCN}$ ), German "Clark 2". It forms colourless prisms of M.P.  $31\text{--}2^\circ\text{C}$ ., having a slight odour of bitter almonds. It has very similar properties to D.A., but is hydrolysed more slowly by water, and is effective in lower concentrations.

(c) *Diphenylamine chlorarsine* (D.M.) ( $\text{N.H: (C}_6\text{H}_4)_2\text{: AsCl}$ ), also termed phenarsazine chloride, or more correctly 10, chloro-5, 10, dihydro-phenarsazine, is sometimes referred to as Adamsite (from the American, Dr. Adams).

When pure it forms yellow, odourless crystals, M.P.  $195^\circ\text{C}$ ., but the technical product is usually greenish-brown in colour. It is practically insoluble in, and unaffected by, water, but is comparatively readily hydrolysed by alkalis, and oxidised by oxidising agents. Crude D.M. corrodes iron, steel, and brass.

#### (8) *Vesicants.*

Mustard gas is the chief member of this group, and was the only one used to any extent during the war, though the potentialities of lewisite and other dichlorarsines were being actively investigated when the war ended. As a group, the vesicants exhibit considerable variation in physical and chemical properties, the dichlorarsine type being, in general, less persistent and less stable than mustard gas, but they all possess the common characteristic of being able to penetrate into and destroy all living tissues with which they come into contact.

(a) *Mustard Gas* (H.S.) (2,2', dichlorodiethyl sulphide;  $\text{S (CH}_2\text{CH}_2\text{Cl)}_2$ ) was known to the French as Yperite, since first used by the Germans at Ypres, on July 12th, 1917; and to the Germans as Senfgas, or Lost, the latter an anagram from the initial letters of Lommel and Steinkopf, who advocated its use to the German Command.

Mustard gas, when pure is a colourless oily liquid of D 1·28, having a faint leek-like odour. It freezes at  $14\cdot4^\circ\text{C}$ . (with tendency to supercool) to long needles, and boils at  $217^\circ\text{C}$ . with decomposition ( $107^\circ\text{C.}/15\text{ mm.}$ ). It has a low vapour pressure (0·11 mm. at  $20^\circ\text{C}$ .) and is accordingly very persistent. The technical product, usually containing 15-20 per cent.



of carbon tetrachloride or chlorobenzene, is a brown or black oil, of variable F.P. (*ca.* 5°C.), having a characteristic odour described as resembling that of mustard, garlic, horse-radish, etc.

It is very sparingly soluble in water (*ca.* 0.06 per cent. at ordinary temperature) in which it sinks, and is slowly hydrolysed to give harmless water-soluble products (thiodiglycol and hydrochloric acid), the hydrolysis being accelerated by heat or the presence of alkalis. It is soluble in most organic solvents, and in animal and vegetable oils, though not so soluble in mineral oils; it is absorbed by rubber, and penetrates into all porous materials, textiles, leather, wood, stone, etc.

It is a comparatively stable compound. Like all organic sulphides it possesses reducing properties, and on oxidation yields the corresponding sulfoxide (m.p. 109-110°C.) and sulphone (m.p. 56-57°C.), both of which are water soluble. The former is physiologically inert, but the latter possesses to some extent the vesicant characteristics of the parent sulphide.

Mustard gas is readily chlorinated to inert substitution products, and its chlorine atoms are relatively reactive, being replaceable by treatment with potassium iodide, sodium sulphide, etc. The pure liquid does not attack metals under ordinary conditions, but the technical product usually contains free hydrochloric acid and has a marked corrosive action on iron and steel.

(b) *Lewisite* (American M-1) 2, chlorovinyl dichlorarsine;  $\text{ClCH}=\text{CH}.\text{AsCl}_2$ ) was developed as a war gas by the Americans towards the end of the war, though never actually tried out in the field, and derives its name from the American Col. Lee-Lewis. It has been termed the "Dew of Death" and claimed to embody the aggressive qualities of the asphyxiants, the irritant characteristics of the tear and nose irritant gases, and the universal action on all tissues of the blister gases.

Pure lewisite is a colourless, oily, and very heavy liquid, having B.P. 190°C. (decomp), and F.P. *ca.* -5°C. (considerable supercooling). It has a vapour pressure of 0.4 mm. at 20°C. and is therefore less persistent than mustard gas. The vapour of the pure compound has only a slight odour, but is markedly irritant to the eyes and nose. The liquid tends to turn blue-black in light. The technical product, which is usually black, has an intolerable geranium-like odour, perceptible in great dilution.

Lewisite is readily soluble in organic solvents and in oils and fats. It is rapidly hydrolysed by water to give the oxide,  $\text{ClCH}=\text{CH}.\text{AsO}$ , which, although somewhat vesicant for direct contact, is much less dangerous than lewisite by reason of its non-volatility and sparing solubility in water and other solvents. A similar hydrolysis takes place in the presence of ammonium hydroxide, but with caustic alkalis the molecule breaks down, with evolution of acetylene.



Lewisite is a very reactive compound, being readily oxidised and chlorinated; and the two chlorine atoms attached to the arsenic are replaceable by treatment with potassium iodide, hydrogen sulphide, etc. It slowly decomposes in contact with iron, but does not appreciably attack steel.

Its action on the skin differs from that of mustard gas in that the liquid "stings", and the irritation develops more rapidly.

(c) *Other dichlorarsines*: *Ethyl dichlorarsine* ( $\text{EtAsCl}_2$ , B.P.  $155^\circ\text{C}$ .) was used to some extent by the Germans during the war, primarily as a lung irritant, under the name of "Dick"; and the corresponding *methyl* compound ( $\text{MeAsCl}_2$ , B.P.  $133^\circ\text{C}$ .) was being actively considered as a war gas by the Americans at the end of the war. They are both relatively volatile, non-persistent liquids having marked lung irritant properties; at the same time they exert a blistering action on the skin, and may therefore be considered as volatile toxic vesicants resembling lewisite in type.

They are colourless, heavy, mobile, oils, having a weak fruity smell, and a pronounced irritant action on the eyes and nose. In general properties they resemble lewisite, but are somewhat more stable, and yield water-soluble oxides on hydrolysis with water or alkalis.

The corresponding *phenyl* compound ( $\text{PhAsCl}_2$ , B.P.  $255^\circ\text{C}$ .) was also used to a limited extent by the Germans, chiefly in admixture with D.C. It is a similar but less volatile, liquid, which is highly toxic, and possesses both respiratory irritant and vesicant properties.

#### (9) *Paralysants*.

Hydrocyanic acid and hydrogen sulphide, the two chief members of this group, were both used during the war, though with very little success. Future use of the latter in warfare is very problematical, but the former may possibly be encountered under certain conditions, and brief consideration will, therefore, be given to it.

*Hydrocyanic acid* (Prussic acid,  $\text{HCN}$ ) under ordinary conditions is a colourless, mobile, and volatile liquid of B.P.  $26.5^\circ\text{C}$ ., having a weak but characteristic odour of bitter almonds, which some individuals, as a personal idiosyncrasy, cannot smell. Its vapour is combustible, burning with a violet flame, and has a density (air = 1) of 0.94. The liquid is miscible with water, but the solution decomposes fairly rapidly, partly to give formic acid and ammonia (especially in the presence of alkali), and partly to give brown polymeric solid products. It is extremely toxic, and many attempts were made during the war to use it successfully, but it suffers from a number of serious disadvantages. Its volatility and low vapour density, for example,



make it very non-persistent, though this can in some measure be overcome by admixture with arsenious or stannic chloride, as in the French Vincennite, V.N.: it is unstable, exhibiting a tendency to polymerise: and it is inflammable and sensitive to explosion.

### CHAPTER III. PRINCIPLES AND METHODS OF GAS DETECTION.

#### (10) *General.*

Gas detection, the recognition of the presence of gas and identification of its type, plays a part of primary importance in passive defence; rapid transmission of information that gas has been used, with details of its nature and of the areas affected, being a very necessary factor of success in Air Raid Precautionary measures.

In general terms the primary functions of the members of the Gas Detection and Identification Service are to detect the presence of gas and recognise its type; to determine approximately the extent of the gas-contaminated area; and, from a consideration of the prevailing weather conditions, to indicate which are the gas-dangerous localities, and advise the authorities accordingly. Further, in case of doubt, it may be necessary for them to take samples of gas-contaminated materials for subsequent chemical examination.

The particular functions of Gas Detection and Identification Officers on any given occasion will naturally depend on circumstances, and on the type of gas encountered. In the case of non-persistent gases and particulate clouds, as already pointed out, little action is usually possible unless they happen to be on the spot at the time of release. Otherwise, by the time they arrive the gas will normally be so dilute as to make identification impossible. There are, however, certain exceptions to this: if, for example, a phosgene bomb happened to fall into an enclosed area, such as a courtyard surrounded by buildings, and the weather was calm, the air in the courtyard might contain a perceptible concentration of phosgene for some 15-30 mins. after release. With bombs containing the less volatile, but still non-persistent, lung irritants, diphosgene and chloropicrin, it will usually be possible to detect the gas in the earth surrounding the bomb crater for many hours afterwards; and even with phosgene this is sometimes possible, especially on a cold day.

As regards the really persistent gases, the persistent lachrymators will, of course, advertise their presence by inducing lachrymation, and further identification will, in general, be superfluous. The persistent vesicants, on the other hand, and mustard gas in particular, constitute the real *raison d'être* of the Gas Detection and Identification Service. From a knowledge of the exceedingly dangerous properties of mustard gas,



it can be readily visualised what would happen if the bursting of even a single mustard gas bomb went undetected. Liquid would be spattered about by the explosion and would slowly evaporate. People in the immediate vicinity would have their eyes, lungs and skin affected by the vapour. Those unfortunate enough to come into contact with the liquid splashes would suffer more severely, and would be potential sources of danger to others with whom they came into contact. Rapid detection of the presence of mustard and other blister gases is essential to avoid this spreading of contamination, and to enable prompt decontamination measures to be put in hand.

## (11) *Methods available.*

The problem of the detection of war gases has been very intensively studied, especially since the war, but despite this no really satisfactory system has yet been devised. The solution of the problem is not, of course, easy. The essential requirements of a method of detection suitable for field use are that it shall be rapid, simple, specific, and sensitive, and the difficulty of combining all four requisites in a single test will doubtless be appreciated. The question of sensitivity is, perhaps, the greatest stumbling block, as the concentrations of gas likely to be encountered in practice are exceedingly small when judged by ordinary standards.

The methods available for the detection of war gases are conveniently considered under two heads, Subjective and Objective, according to whether the senses alone are employed as testing instruments, or use made of some external physical or chemical aid. The smell, appearance, and physiological effects of the gas concerned come, of course, under the Subjective heading, whilst as an example of a typical Objective test may be instanced the colour-change of an impregnated test-paper in the presence of the gas.

In general, none of the available methods is entirely satisfactory *per se*, but taken all together they usually afford a reliable indication of the nature of the gas present. For rapid recognition in the field—and rapidity is essential—subjective tests are normally of greater value than objective, but the latter are on occasion very useful adjuncts, especially for confirmatory purposes.

## (12) *Subjective methods of detection.*

(a) *Smell.* The most important of the subjective methods of detection is the sense of smell. The majority of the gases used in warfare, as noted above, have a distinctive smell, which in many cases is perceptible in low and relatively harmless concentrations (*v.* Table II). Under favourable conditions, for



example, mustard gas can be detected by smell in concentrations as low as 1 in 20 million; while the geranium-like odour of crude lewisite is perceptible in even greater dilutions.

The sense of smell is, however, liable to be erratic in action, and subject to personal idiosyncrasy, its sensitivity varying considerably from individual to individual, some, indeed, being incapable of perceiving certain odours, such as those of mustard gas or hydrocyanic acid, at all. Even with the same individual, the sense of smell has "off" days, and is, of course, completely put out of action by a cold in the head, or by the presence in the atmosphere of a potent nose irritant. Even under "good" smelling conditions the sense of smell soon tires and gets accustomed to odours, so that after a time it may fail to detect the presence of gas in relatively low but nevertheless harmful concentrations. On the other hand, it may vaguely register the presence of an odour but be unable to identify it, and, of course, if the smell of the gas is masked by other odours—a not infrequent occurrence under war conditions—it fails completely, for it is one of the major limitations of the sense of smell that it has a very poor ability to separate mixed odours.

A chemist's nose is usually rather better suited for the task of gas detection by smell than those of other individuals, but even so it requires a certain amount of training to develop odour-memory and ability to differentiate between odours, locate their source, and so on. The Germans, in common with other continental races, have devoted considerable attention to the training of the sense of smell as a means of detecting war gases. As one authority says, "The Gas Scout should possess a well-educated nose—one that has been taught to smell dangers, as the eye has learnt to see them and the ear to hear them". They have embodied the results of their experience in the form of six principles, which are given below, as they effectively summarise the more important points to be borne in mind when using the sense of smell for purposes of gas detection and identification.

- (1) Don't inhale deeply: only the nose can smell: sniff!
- (2) Only smell once: repeated smelling dulls the perception.
- (3) First smell, then reflect: ability to recollect smells can be acquired with practice. Learn smells by heart.
- (4) After smelling, breathe out strongly through the nose several times. Don't make a new smell-test until the effects of the last have disappeared.
- (5) Don't smoke while smelling: smoking dulls the perception.

One exception to this rule is, perhaps, allowable. Even slight traces of phosgene so affect the taste nerves that tobacco smoke acquires a flat, metallic taste, and becomes disagreeable and



repugnant. This characteristic, much used during the war, and known as the " Tobacco reaction ", is not peculiar to phosgene alone—hydrocyanic acid and hydrogen sulphide have the same property to a lesser degree—but may occasionally be found useful as confirmatory evidence.

(6) Name each odour-perception. A thing is only odourless when no perception is sensed.

In the event of the Gas Identification Officer encountering an unrecognisable smell, it is most important that his description should be as accurate and comprehensive as possible. Information to the effect that no odour is perceptible may be of value.

It is, perhaps, unnecessary to add that smell-tests in the field should be made downwind, and, when wearing the respirator, by turning the back of the head to the wind, inserting the fingers between the facepiece and the cheek, and sniffing gently. The tendency of gases and vapours to rise as they drift downwind should also be borne in mind, and care taken to make smell-tests with the face close to the ground when endeavouring to locate the source of contamination.

(b) *Sight*.—The sense of sight is, perhaps, of equal importance for gas detection purposes to that of smell, particularly in connection with persistent gases.

With non-persistent gases circumstances may sometimes arise where visual indications are of value. A concentrated cloud of chlorine, for example, has the characteristic yellow-green colour of that element, unless there is much moisture in the atmosphere when it appears whitish owing to condensation. Phosgene and diphosgene vapours similarly give whitish clouds under damp conditions, but are colourless and invisible if dry; whilst particulate arsenical smokes, as the name indicates, are white and opaque if sufficiently concentrated, as for instance in close proximity to a generator, though invisible when dilute. Conversely, however, a white cloud does not invariably indicate the presence of poison gas—it may be artificial smoke deliberately produced for screening purposes, or incidental smoke arising from the use of incendiary and other bombs. It is, nevertheless, prudent to suspect all unusual clouds and smokes as possibly containing gas, and take steps accordingly.

In general, such non-persistent gases and smokes will have dissipated to a greater or lesser extent before the Gas Identification Officer arrives, leaving possibly a slight odour behind, and possibly also a certain amount of visual evidence in the form of rotted clothing and bleached vegetation, or corroded metals, particularly copper and copper alloys (notably with the lung irritants in damp weather). The size of the crater made by the bombs may also point to the use of gas, the cratering produced by H.E. bombs being usually considerably deeper and more extensive than that from gas bombs.



With persistent gases, on the other hand, and mustard gas in particular, smell may or may not afford a reliable indication, according to the prevailing circumstances, but contamination of ground and/or buildings with the liquid gas will invariably occur, and so afford visual evidence of the presence of the gas.

Contamination by crude mustard gas, of black colour, is naturally somewhat easier to detect visually than contamination with the purer pale yellow product, though apart from colour the "stains" produced by both have much the same appearance. On dry porous surfaces, brickwork, cement, stonework and so on, the liquid is rapidly absorbed, leaving a dark oily stain. On dry roads and dry earth it similarly appears as a wet oily patch, whilst on wet surfaces it spreads and gives a slight iridescent effect, similar to that of paraffin on such surfaces. It rapidly penetrates bare wood, especially along the grain, but remains as liquid drops and splashes on painted surfaces for a considerable time, though it tends eventually to soften and dissolve in the paint film. It does not penetrate into metals, glazed tiles, and similar impermeable materials, and also remains in droplet form on green foliage and grass for some time, though it eventually penetrates into and damages living vegetation. In water the bulk sinks to the bottom, but a thin, somewhat iridescent film usually remains on the surface for a time.

These remarks apply, for the most part, to the zone of relatively gross contamination in the immediate vicinity of a bomb crater. The lighter contamination further away, and also the contamination resulting from aircraft spray, takes the form of very small (sometimes pin-point) droplets, and is, naturally, less apparent, and accordingly more difficult to detect visually, (cf. Section (13) (b) below). In the form of a mist, these minute droplets may drift for considerable distances downwind from the point of release.

A word of warning is necessary in connection with the visual detection of blister gas contamination; the persistent lachrymators are dark-coloured oils similar in appearance to crude blister gases, and care must be taken not to confuse the two types—a relatively easy matter if the Gas Identification Officer is wearing a respirator, and omits to make periodic smelling tests.

(c) *Other Senses*.—The other senses are not of particular value from the gas detection point of view, but the circumstance that gas projectiles normally burst with much less violence than H.E., and do not flame like Incendiary, is worth bearing in mind. It may also be mentioned that the hissing noise of gas escaping from cylinders occasionally afforded a valuable warning during the war, though this method of release is not, of course, likely to be encountered in aerial attack.



(d) *Physiological Effects*.—The physiological action of war gases affords a valuable warning indication in the case of those which exert an immediate irritation on some part of the body. Lachrymators, for example, are readily recognised by their immediate irritant effect on the eyes even in very low concentrations (1 in 20 to 30 million). In the same way, the nose irritants give rise to their characteristic, though slightly delayed, irritation of the nose, throat, and chest, in even lower concentrations (1 in 100 million or less). With these smokes, in fact, which are practically odourless in such dilutions, physiological detection in this way is the only practicable field method.

Amongst the lung irritants, chloropicrin betrays its presence by lachrymatory effects in relatively low concentrations, and like chlorine is intolerable to breathe even in concentrations which are relatively harmless. With phosgene and diphosgene, on the other hand, the irritant effects are far less marked, and concentrations which are detectable by smell and slight irritation of the breathing passages are *not* intolerable to breathe, but may lead to serious results if breathed for any length of time. Further, the intensity of the physiological effects, cough and so on, affords little indication of the magnitude of the concentration involved. To wait for physiological indications in the case of such gases is, obviously, inviting disaster.

Similar remarks apply with even greater force to mustard gas, which has a characteristic delayed action and produces no immediately recognisable symptoms. The arsenical vesicants, lewisite and so on, have, however, an immediate irritant effect on the nose and eyes, which can serve as a warning indication.

Certain toxic gases, notably the odourless and non-irritant carbon monoxide, can, as is well known, be detected in sub-dangerous concentrations by means of their physiological action on small sensitive animals, etc., exposed to the suspected atmosphere. This procedure, however, though possibly of value under certain circumstances, has obvious limitations, and is not suited for general application under war conditions.

### (13) *Objective methods of detection.*

A large number of different types of objective methods of detection have been proposed from time to time, but the majority of them fail to fulfil the four essential requirements referred to above, namely that they must be simple, rapid, specific, and sensitive.

(a) *Physical and physico-chemical methods*.—On the purely physical side it has been proposed to detect the presence of war gases in air by measuring the slightly altered physical properties (refractive index, rate of diffusion, electrical conductivity, and so on) of the air-plus-gas mixture: or, alternatively, by absorbing the gas on a fatty or other medium and observing



the alteration in physical characteristics of the latter. All such methods, however, are unspecific—they merely indicate the presence of some impurity in the air; the apparatus required is frequently complicated and cumbersome; and corrections have normally to be applied to compensate for variation in atmospheric conditions.

Similar objections apply, for the most part, to the majority of the proposed physico-chemical methods. Spectrographic detection, for example, though specific and sensitive is hardly suited to field work. On the other hand, its more simple modification—Beilstein's flame test for halogens—was used as a Lantern test during the war, and might conceivably be so used again. It is, of course, unspecific, being based on the formation of volatile copper halides when halogenated compounds are decomposed by heat in the presence of copper, but is reasonably sensitive, and can be made more or less automatic in action.

Another variety of physico-chemical test which has been proposed is based on the alteration that takes place in the temperature or luminosity of a controlled flame or heated wire when combustible gases are present in the air. This, however, is obviously more suited to the detection of carbon monoxide and other readily combustible gases than of war gases, and is, in any case, unspecific and relatively insensitive.

Finally, as a matter of historical interest, passing reference may be made to the war-time attempts to indicate electrically the approach of a chlorine cloud by means of its depolarising action on a polarised voltaic cell, or its effect on the resistance of a bare wire forming part of an accurately balanced circuit, though these were not very successful owing to the invariable time lag of such systems.

(b) *Detector paint*.—For assisting in the delineation of areas contaminated with liquid blister gas, indicators have been devised known as "Detectors, Ground", consisting of paper, or other material, painted with a special yellow-coloured paint which turns red in contact with the liquid gas. The principle underlying this method of indication, which is fairly generally known and utilised in other countries (*cf.* Section (18)), consists, in general terms, in the incorporation in the paint of a small quantity of a suitable chemical which is dissolved out by contact with liquid blister gas to give a red solution.

It will be evident, therefore, that the detector paint has several definite limitations. In the first place, it is not specific to blister gases: the majority of ordinary solvents and oils (alcohol, benzene, carbon tetrachloride, petrol, paraffin, lubricating oil, etc.) have little or no effect on it, but on the other hand, a few, such as acetone, nitrobenzene, and pyridine, and also certain of the persistent lachrymators (*e.g.*, K.S.K. and B.B.C.) react in the same way as do the blister gases, giving



bright red colourations. In the second place, a positive reaction is only given by *liquid* contamination: contact with vapour can not dissolve out the chemical. And in the third place, the red colouration produced is not always very perceptible with the crude black form of blister gas (except at the edges of the liquid stain), and when the detector paper is used by pressing it into contact with a surface suspected of being contaminated, the colouration may be obscured by dirt, tar, oil and so on.

In spite of these limitations, however, the "Detector, Ground" may on occasion be of definite value. Tests with the paper must, however, be carried out before the liquid spots and splashes have been completely absorbed: if liquid as such is still present in the upper layers of the contaminated material, the paper will give a positive reaction when pressed up against it, but no red colouration will be obtained if the material is superficially dry.

A similar type of detector is used for the detection of persistent gas spray from aircraft, metal panels painted with the detector paint ("Detector, Spray") being exposed, paint uppermost, in open places. Arrival of spray will be indicated by the appearance of red spots on the painted surface, and this, normally, will be the only immediately available evidence that such spraying has occurred.

(c) *Chemical methods*.—Chemical methods of gas detection, like all qualitative chemical tests, are based on reactions involving the formation of insoluble or highly coloured products.

Since many of the war gases contain a hydrolysable halogen atom, the simplest, but least specific, of such chemical tests is one depending on the colour change of a suitable acidimetric indicator. It has been suggested, for example, that the suspected air should be tested with congo-red paper, or bubbled through a solution of bromothymol blue: or alternatively, in the case of persistent gases, that a pad impregnated with methyl red should be pressed into contact with materials suspected of being contaminated. Readily hydrolysable gases, such as diphosgene and lewisite, give a fairly rapid colour change under these conditions, but the change is much slower with mustard gas, and does not, of course, occur at all with a stable compound such as chloropicrin. The method also suffers from the great disadvantage of being affected by all extraneous acids that may be present in the atmosphere.

In the same way, and subject to similar limitations, the suspected air may be passed through an alcoholic solution of silver nitrate, and the presence of readily hydrolysable, halogen-containing war gases detected nephelometrically. Pyrolysis of war gas vapours by passage through a red-hot silica tube, and subsequent detection of the breakdown products (hydrochloric acid, *inter alia*) has also been suggested.



The ideal chemical method is one involving the colour change of an impregnated test paper. For certain industrial gases this method is possible, but for the majority of war gases paper tests are either not available, or are insufficiently specific or sensitive, and one has to fall back on the more general method of passing the suspected air through a suitable solvent or absorbent (a filter in the case of particulate clouds) and applying the reaction to the latter. This general method, despite obvious defects, is not without its value in gas identification work, as it enables the gas to be stored up in an artificially concentrated condition, and if required, taken away for identification to the more convenient surroundings of a laboratory.

Chemical methods of detection are, of course, capable of giving accurate and definite information, but few of them can be described as rapid and simple, and their application in the field is rarely practicable on account of the amount of apparatus and reagents required.

#### (14) *Field testing and sampling.*

Experience has shown that under active service conditions reliance must be placed almost exclusively on subjective indications for effecting a rapid diagnosis on the spot of the type of gas present, and that confirmatory objective tests can, in general, only be satisfactorily applied in a laboratory on samples of contaminated materials collected for the purpose.

The contents of the testing and sampling equipment to be issued to Gas Identification Officers have, therefore, been restricted to

(a) Apparatus and reagents for testing for the presence of mustard gas—the most dangerous and insidious war gas, and the one most likely to be encountered; and

(b) Equipment for taking samples of materials contaminated with an unidentifiable persistent gas for subsequent chemical examination.

A supply of detector paper for use in the delineation of contaminated areas, etc., and means for sampling vapours and particulate clouds, have also been included, though it is doubtful whether much use will be found for the latter.

The method of use of the equipment is fully described in Appendix I.



## CHAPTER IV. DUTIES AND RESPONSIBILITIES OF GAS IDENTIFICATION OFFICERS.

### (15) *Organisation of the Gas Detection and Identification Service.*

The organisation of the Gas Detection and Identification Service is dealt with in A.R.P. Memorandum No. 11 and need not be detailed here.

Briefly, the initial responsibility for detecting the presence of gas will rest on air-raid wardens (or, in their absence, on members of such other services as may be on the spot), but a number of specialist Gas Identification Officers (G.I.O.'s), recruited from persons of suitable professional qualifications and given special training in the detection and identification of war gases, are to be available to act as gas-identification consultants. These Officers will have no executive authority, their status being solely that of expert advisers responsible primarily for confirming the presence and nature of the gas reported, and advising on the extent and duration of the danger. Each G.I.O. will be provided with an assistant.

A G.I.O. will normally remain at his ordinary work or at home and will be required, on receipt of information of a gas attack, to proceed at once to the area affected either via a depot or direct, according to local arrangements.

### (16) *Duties of Gas Identification Officers.*

(a) *General.*—In general terms the duties of a Gas Identification Officer, on receiving notification from his Report Centre of a gas attack, will be to proceed to the spot to confirm the presence and nature of the gas reported. His opinion on these points will have to be communicated to the services on the spot, and he should also be prepared to advise on the extent and duration of the danger, to ensure that adequate precautionary measures are taken.

In addition he will, of course, have to report his conclusions as clearly, concisely, and rapidly as possible to the Report Centre (*v.* Appendix II).

Having made his report, and, if doubtful of the nature of the gas, taken a sample of contaminated material for subsequent examination, the G.I.O.'s responsibility would be ended so far as that particular locality was concerned. He would not be responsible for ordering or supervising decontamination, evacuation, first aid, etc.



In addition to his special apparatus each G.I.O. will be supplied with a respirator and full anti-gas clothing (including helmet and curtain), which will normally be worn whilst on active duty. Where the G.I.O. is to go direct to a contaminated area from his home or place of business, he will need to keep his protective clothing and apparatus himself so that he may be ready to set out immediately he is called upon.

After a tour of duty, the G.I.O. will proceed, if necessary, to the depot for cleansing and decontamination. The cleaning and decontamination of the special apparatus should always be carried out by the G.I.O. himself. A spare suit of clothes for each G.I.O. should always be available at the appropriate depot.

(b) *Approach to gassed area.*—The G.I.O., having if necessary been conveyed or guided to the neighbourhood of the reported gas contamination, should approach the area warily, with all his senses keen and alert. It is one of the most fundamental duties of all concerned in the Anti-gas Organisation not to get themselves contaminated or become casualties through carelessness. If they do, they are, of course, unable to carry out their particular tasks, and at the same time are putting an unnecessary strain on the first-aid services.

Accordingly, although the G.I.O. will make his first smelling tests and so on as he approaches the scene with his respirator at the alert, he must put the latter on immediately a suspected odour is encountered or irritation of the eyes or nose is experienced, and thereafter make periodic smelling tests in the normal manner (*v. Sect. (12) (a)*).

Similarly he should maintain a watchful eye for ground contamination and avoid blundering into it unnecessarily; and must bear in mind the possibility of there being drops of liquid gas on foliage, walls and so on, and avoid unnecessary contact with them.

(c) *Diagnosis of type.*—The primary function of a G.I.O. is, as repeatedly emphasized, to effect a rapid diagnosis of the type, and if possible the identity, of the gas present. To do this he must, for the most part, rely on subjective indications, which will, at any rate, enable him to distinguish broadly between (i) the non-persistent gases, (ii) the persistent lachrymators, and (iii) the persistent vesicants.

(i) *The non-persistent gases* will afford little or no visual evidence of liquid contamination, but will be indicated by marked lachrymation in the case of C.A.P., by nose and throat irritation in the case of the arsenical smokes, and by some characteristic irritant smell and other symptoms in the case of the lung irritants.



The action to be taken by the G.I.O. when non-persistent gases are encountered will depend on circumstances, particularly the time that has elapsed since the gas was released. If he is very rapidly on the scene, especially in calm weather, it should be possible for him to recognise the gas present; but if some time has elapsed, or the weather is rough, this may not be possible. In either case, he will have to report his conclusions to the Report Centre, and if gas is still present in appreciable quantity, endeavour to estimate the danger of the situation and give such advice as may be necessary concerning the appropriate precautionary measures.

(ii) *The persistent lachrymators* will be indicated by visual evidence of liquid contamination accompanied by intense lachrymation. Apart from reporting the nature, location, and extent of the contamination to the Report Centre and giving advice on the spot, little further action will usually be necessary—unless there is any reason to suspect that blister gas is admixed with the lachrymator, in which case a sample of contaminated material should be tested for the presence of mustard gas as described in Appendix I.

(iii) *The persistent vesicants* will be indicated by liquid contamination accompanied, in general, by a characteristic odour, but no marked lachrymation. Whether it is mustard gas or vesicant of the lewisite type will usually be evident from the smell and the immediate nose irritant effect of the latter, but the presence of mustard gas can, if necessary, be confirmed by testing as above.

The action to be taken when blister gas is encountered or suspected will be to ascertain the approximate extent of the area heavily contaminated with the liquid gas, to estimate as far as possible the danger arising from the vapour, and, after giving advice on these matters to those on the spot so that immediate steps may be taken to rope off and mark the dangerous areas and if necessary evacuate buildings downwind, report fully to the Report Centre.

(d) *Delineation of contaminated areas.*—In estimating the extent of an area contaminated with a persistent gas, no attempt should be made to effect an accurate delineation by groping round the periphery with detector paper. All that is required from the G.I.O. is a broad indication of the area affected; in the case of a persistent gas bomb falling in a street, for example, that the crater was at X, and that the zone of heavy contamination extended roughly from points A to B in that street. Detector paper may occasionally be useful for deciding whether apparent liquid contamination is really a persistent war gas or merely lubricating oil, water, etc., but it should not be used unnecessarily as a routine duty.



As far as possible the G.I.O. should avoid walking about over grossly contaminated ground, but if this is really necessary (as, *e.g.*, for the purpose of taking a ground sample), he should subsequently remove as much surface contamination as possible from his boots by well wiping them, doormat fashion, in dust or other available absorbent material, so as not to spread the contamination when proceeding to other areas.

(e) *Assessment of danger*.—In estimating the danger to be apprehended from the presence of gas, consideration must be given primarily to the nature and location of the gas, and to the prevailing weather conditions, particularly the direction and velocity of the wind.

With non-persistent gases, as previously mentioned, the gas will normally be dispersed before the G.I.O. arrives on the scene, especially if the wind is strong. In the comparative absence of wind, however, the rate of dilution of a non-persistent gas with the surrounding air may be relatively slow, and in such cases, it should be possible for the Officer to give advice on the spot as to the areas which are likely to be affected by the gas as it drifts slowly downwind, and, from a consideration of the nature and approximate concentration of the gas, to advise, if necessary, on the precautions to be taken.

In the same way, and through the same channels, warnings can be given in localities downwind of an area contaminated with a persistent gas: the vapour danger in this case being greatest in hot weather, and persisting until the area concerned has been freed from liquid gas by the application of adequate decontamination measures, or failing that, by natural evaporation over a period of several days.

With such persistent gases, and more particularly the blister gases, it is, of course, essential that all access to the area heavily contaminated with liquid gas should be prevented by roping off and the erection of the recognised warning signs. The urgency for applying decontamination treatment to such areas will depend on local circumstances, and no hard and fast rules can be laid down. As a basic principle, however, it is evident that blister gas contamination should, in general, receive prior consideration, and that contaminated areas which can be readily roped off and avoided (*e.g.*, those in open playing fields, etc.) should be regarded as less dangerous and requiring less urgent decontamination treatment than those where such action is impracticable.

The general situation arising from the presence of gas, and the relative urgency of treatment, can, however, only be fully appreciated at the Control Centre; the primary responsibility of G.I.O.'s is identification of the gas present.



(f) *Samples for subsequent examination.*—If doubtful of the nature of the gas present, the G.I.O., in addition to reporting the fact to the Report Centre, should take a sample of the gas and/or contaminated material. The sample should be retained pending further instructions, but at the earliest opportunity the G.I.O. should report to the Senior Gas Adviser for the area, giving the fullest possible details of all the circumstances, including any information he has been able to obtain from the local medical authorities, regarding the symptoms present in victims of the gas in question.

The Senior Gas Adviser will consider this report in conjunction with any relevant information from other sources, and decide what further action is required. He may decide from the fuller information available to him that one of the known gases is involved, but that identification has been rendered difficult by some special circumstance, in which case he will endeavour to confirm this by examination of part of the sample collected by the G.I.O. If, however, the evidence indicates that there is a probability of a new gas having been used, the procedure described in Section (17) (a) will be adopted.

Samples for subsequent examination should be taken in all cases presenting inexplicable features. At the same time, however, the G.I.O. should bear in mind that his supply of sample bottles is limited, and avoid filling them unnecessarily with samples taken merely to confirm reasonably definite subjective indications.

(g) *Aircraft spray.*—The foregoing remarks apply for the most part to air raids involving the use of gas bombs. In the case of contamination by spray from aircraft the G.I.O.'s task will be rather different. The "Detector, Spray" will function as a silent alarm, affording a warning that spraying has occurred, and all the G.I.O. can do is to confirm the probability that the liquid sprayed was mustard gas. In general it will be possible to do this by making a vapour test in a locality which is visibly contaminated by spray, as *e.g.*, immediately above a detector panel which is heavily "spotted".

No useful samples of contaminated material will normally be obtained, but if an element of doubt exists, it may be possible to treat the spray detector itself as a contaminated sample, the paint on the red spotted areas being scraped off and placed in a sample bottle.

(h) *General duties.*—Apart from the specific duties already described G.I.O.'s may be called upon by local authorities for general advice on any problems of gas contamination.

It is evident, therefore, that even if rarely called upon to use it, G.I.O.'s should possess a comprehensive knowledge of the properties of the different war gases, their effect on various



materials, and the methods available for their destruction. This aspect of the G.I.O.'s work is dealt with in the following chapter.

(17) *The Element of Surprise in gas warfare.*

In all his work the G.I.O. must bear in mind the importance of the element of surprise in warfare, and be constantly on the look-out for new factors.

(a) *New Gases.*—The use of new gases in war is, of course, quite possible, perhaps even probable: but such new gases are more likely to be more efficient modifications of the present types than complete innovations.

The function of a G.I.O. in the event of a new or unidentifiable gas being encountered has already been briefly referred to (Section (16) (f)). In addition to reporting the fact immediately to the local Report Centre, he should, at the earliest possible opportunity, submit to the Senior Gas Adviser a comprehensive and accurate report of the peculiarities and chief characteristics (smell, appearance, physiological effects, behaviour towards reagents, etc.) of the "new" gas, and if possible secure a sample either of material heavily contaminated with it, or better still, the contents of an unexploded bomb suspected of containing it. If the new gas is very volatile and non-persistent, the obtaining of a sample may be a difficult matter unless evacuated gas bottles, or gas pipettes, are available: even a vapour sample collected on charcoal may, however, be of some value. The fact that a strange gas is suspected should be regarded as confidential, and the samples retained pending further instructions.

If the Senior Gas Adviser decides from the available evidence that there is a probability of a new gas having been used, he will ask the G.I.O. to forward the samples and will then, if he judges it necessary, forward them for examination at a central laboratory in accordance with arrangements made by the Ministry of Home Security. This procedure has been adopted because the early identification of any possible new gas is a matter of national importance, affecting not only the local public, but the public at large and also the defence services. It is essential, therefore, that all such information should be considered centrally, and analytical investigations carried out at a laboratory staffed by experts with wide knowledge and experience of substances likely to be used. Local investigations by anyone other than such an expert might result in incorrect conclusions and possible wastage of valuable samples. Moreover, the introduction of a new gas might on occasion necessitate the revision of certain protective measures, and recommendations on this point can only be made by a central authority.

The taking of such samples, and their packing for despatch, is dealt with in Appendix I. If the sample takes the form of



an unexploded bomb, expert military advice should be sought as to how to render it safe for transport.

During the Great War a comparatively large number of different gases was used, more or less experimentally, from time to time. Since the war these efforts to find serviceable and more potent gases have been continued in various countries, the general trend of such researches being, broadly speaking,

(a) to find a gas against which existing types of respirator are useless;

(b) to combine in one gas the aggressive properties of several existing types ("multiple effect"); and

(c) to discover a gas having a different mode of action on the body.

With regard to the first of these, the possibility of making carbon monoxide a useful war gas is still being considered in various countries. There are, however, many practical difficulties in the way, and no matter how used, carbon monoxide remains a very non-persistent gas, and relatively speaking a not exceptionally poisonous one. Various suggestions have been made regarding the possibility of developing toxic smokes containing particles of such dimensions that they would either penetrate, or else clog up, the ordinary types of particulate filter; but here again there are considerable practical difficulties in the way, notably that of maintaining the necessary high concentrations. There have also been reports of other "mask-breakers", capable of penetrating all known types of respirator, though in this connection attention has also been drawn to the axiom that gases against which protection is impossible, could never be satisfactorily employed in warfare owing to the danger to the user.

Of the "multiple effect" gases having toxic, irritant, and vesicant properties combined, passing reference may be made to the alkyl dichlorarsines (*v.* Section (8) (c)); and to phosgene oxime,  $\text{Cl}_2\text{C}=\text{N.OH}$ , and nitroxyl fluoride,  $\text{NO}_3\text{F}$ , the two latter being both exceedingly unpleasant substances, but, fortunately, too unstable to be of practical value.

In the last category, gases having a different mode of action on the body, mention may be made of lead tetraethyl,  $\text{PbEt}_4$ , the highly toxic "anti-knock" compound; diethyl telluride,  $\text{Et}_2\text{Te}$ , and similar compounds, which as liquid or concentrated vapour are capable of exerting a toxic action following absorption through the skin. There are also the so-called prickling gases, such as o-chlorobenzal malonodinitrile,  $\text{ClC}_6\text{H}_4.\text{CH}=\text{C}(\text{CN})_2$ , which function like C.A.P. in strong concentrations, by irritating the skin and setting up an intolerable itching and burning sensation, and differ from vesicants in that the irritation is only temporary, no slow-healing blisters being formed. None of these, however, are considered by competent authorities to be of any particular value as war gases.



(b) *Modification by admixture, etc.*—Apart from bearing in mind the possibility of encountering new gases, it is perhaps even more important for the G.I.O. to appreciate that the enemy may, and probably will, try to make his attacks more effective by concealing the fact that gas has been used and the nature of the actual gas employed.

The properties of a liquid, as is well known, depend to a considerable extent on its degree of purity, and can be materially modified by admixture with other substances. Although, therefore, the G.I.O. is familiar with the appearance and so on of mustard gas as normally used, he must not imagine that it will invariably present the same characteristics. It may possibly be used in a more pure form as a colourless oil with a less pronounced odour; it may be made more oily (even ointment-like) and more persistent by admixture with oils and greases; its smell may be disguised by the addition of a powerful odorant (nitrobenzene and citronellol were experimented with during the war), or masked by admixture with a persistent lachrymator such as B.B.C.

Alternatively, of course, the enemy may succeed in temporarily dislocating the normal life of a community by using a liquid that simulates mustard gas in appearance, and possibly even in smell, but is really a relatively harmless "swindle gas". (cf. the use of butyl mercaptan by the French, and of "Stink bombs" containing bone oil or balloon dope by the British, during the war.)

Similarly, just as during the war phosgene was mixed with arsenious chloride, chloropicrin, and so on to increase its persistence, so other mixtures of war gases will probably be met with under certain conditions. Mixtures of mustard gas and lewisite, and of B.B.C. and chloropicrin, have, for example, been considered in certain countries for use under cold climatic conditions to obviate freezing. There is also the possibility of absorbing mustard gas and other war gases on Kieselguhr, and disseminating the resulting highly dangerous mixture in the form of a fine powder.

Even without such complications the task of the G.I.O. will not normally be a light one, owing to the very difficult conditions under which he will have to work. Air raids of the future, many of which may occur at night, will almost certainly involve the use of High Explosive, Incendiary, and Gas Bombs in combination—giving, of course, a variety of incidental odours, etc., in the atmosphere, and thereby greatly increasing the difficulty of detecting the presence of gas.

#### (18) *Foreign Gas Detection Services.*

Other countries are, naturally, faced with precisely the same problems, and gas detection services are now a normal part of the A.R.P. organizations.



Considerable importance is placed on the training of "Scouts" with highly developed sense of smell (French "Eclaireurs Z": German "Gasspürer"), and in many countries instructional material for the practical recognition of war gases—smelling bottles, impregnated matches, etc.—has been available for some years. In certain countries, also, special respirators incorporating "Sniffing valves" have been produced for the use of such scouts, to enable them to make smelling tests easily and safely.

The utility of some kind of liquid-gas detector, similar in principle to our detector paint is also appreciated. The Germans, for example, use a paper impregnated with a Sudan dye, which dissolves out to a red solution in contact with liquid mustard gas (and the majority of organic solvents) and to a blue-purple solution in contact with liquid lewisite. The Russians have detector papers of a somewhat similar type. The Germans also have dye-chalk on the same principle, which is applied by sprinkling the mixed powder over spots suspected of being contaminated—not too much, of course, or the colour development is buried. Sudan-chalk dusting powders are likewise used by the Dutch and Swiss, whilst the Swedes have a similar powder incorporating a blue dye. The French, on the other hand, prefer the acidimetric type of detector, and employ "Bruère's Plug", which consists essentially of a plug of cotton wool impregnated with a solution of methyl red, and when moistened with water and pressed against the contaminated spot, turns rose-red if mustard gas, lewisite, or other more or less readily hydrolysable gas (or acid substance) is present (*cf.* Sect. (13) (c)).

As regards chemical detection and identification, opinions differ considerably in different countries as to the advisability of attempting to take and identify vapour samples on the spot. In some types of apparatus, *e.g.*, the French "Prolabo" Detector, provision is made for the detection (by paper test) of many somewhat improbable gases, such as hydrogen sulphide, hydrocyanic acid, arsine, and so on. In others a non-specific acidimetric or oxidation reaction is utilised for the detection of war gases in general. Only in a few, such as the bulky Russian "G.4" apparatus, is an attempt made to provide for the chemical identification of all the more important war gases; the general tendency, as exemplified by the German "D.S." apparatus, being to provide only for the identification of mustard gas vapour. The necessity of taking samples of materials contaminated with unidentifiable gases for subsequent laboratory examination is, however, universally recognised.



## CHAPTER V: CHEMICAL IDENTIFICATION OF WAR GASES.

Under active service conditions, it is improbable that G.I.O.'s will normally have either time or opportunity for carrying out chemical work on the identification of war gases, apart from such tests as are included in their portable equipment. As expert advisers to the local authorities, however, it is essential that they should be thoroughly conversant with the characteristics of the gases likely to be encountered, so as to be in a position to offer advice, or to undertake such work if called upon to do so. A brief résumé of the methods available for the chemical identification of the more important gases, and of the laboratory technique employed in the handling of contaminated materials is, therefore, given below.

### (19) *Chemical Reactions of the war gases.*

(a) *Lung Irritants*.—The majority of the lung irritants possess characteristic odours and irritant effects by means of which they may be recognised in the field, but samples for subsequent examination will not normally be obtained owing to their non-persistence.

(i) *Chlorine*: For the identification of chlorine the usual tests, depending either on its oxidising properties (*e.g.*, blue colour with aniline acetate: yellow colour with *o*-tolidine hydrochloride), or on its power of liberating other halogens from their compounds (*e.g.*, iodide-starch, and bromide-fluorescein papers), are available.

(ii) *Phosgene*: and (iii) *Diphosgene*: These two gases are chemically similar, and can be detected by means of papers impregnated with a solution of 5 gms. *p*-dimethylamino benzaldehyde and 5 gms. diphenylamine in 100 c.c. of alcohol, such papers (used dry) changing colour rapidly from white to yellow or orange in the presence of as little as one part of phosgene in a million parts of air. The papers are, however, somewhat sensitive to light, necessitating storage in the dark, and are not specific, a similar reaction being given by hydrochloric acid and moist chlorine. For the detection of phosgene, therefore, they should be used in conjunction with a guard-tube containing pumice granules impregnated with sodium thiosulphate and sodium iodide, which react with and remove the interfering gases.

A specific test for phosgene and diphosgene is the formation of a white turbidity or precipitate of diphenyl urea,  $\text{CO}(\text{NHPh})_2$ , m.p.  $236^\circ \text{C.}$ , by passing their vapours through a saturated aqueous solution of aniline. This reaction will



detect 0.2 mgm. of phosgene, and can be applied quantitatively by weighing the precipitated diphenyl urea after washing and drying at 70° C.

Both phosgene and diphosgene are rapidly hydrolysed by water, and are readily destroyed by reaction with alkalis, amines (particularly hexamine), and alkaline solutions of phenols.

(iv) *Chloropicrin*.—For the detection of chloropicrin, papers impregnated with a 5 per cent. solution of dimethyl aniline in benzene have been suggested, but the colour change (white to yellow) which occurs in the presence of chloropicrin is only marked in strong concentrations, or preferably in contact with the liquid gas.

The most characteristic chemical test for chloropicrin is that depending on the formation of nitrite as a product of hydrolysis with alcoholic sodium ethoxide.

Other reactions suitable for the identification of chloropicrin include, pyrolysis in a hot silica tube to form phosgene, nitrosyl chloride, and other products; production of an insoluble precipitate with alcoholic sodium thiophenate solution; and the formation of chloroform as a product of hydrolysis with alcoholic alkali, the chloroform being subsequently identified by its colour reactions with thymol, resorcinol, etc.

Chloropicrin is a relatively stable substance, almost insoluble in water, and unaffected by acids and alkalis. It is, however, rapidly destroyed by alcoholic alkali, or alkaline polysulphide solutions, and also by treatment with a hot concentrated aqueous-alcoholic solution of sodium sulphite. The latter reaction can be used quantitatively, by estimation of the chloride produced.

(b) *Lachrymators*.—The lachrymators as a class are, perhaps, the most difficult of all the war gases to identify chemically, though they are, of course, readily detectable by their physiological effects, and in many instances identifiable by their characteristic odours. They are all rapidly destroyed by hydrolysis with alcoholic alkali, and for the most part attacked by strong oxidising agents; and examination of the products of hydrolysis or oxidation is, in general, the only satisfactory procedure for their chemical identification.

(i) *Xylyl bromide*: The following test, depending on the invariable presence of the *o*-isomer in the mixture, was developed during the war. Oxidation with alkaline permanganate gives the corresponding phthalic acids, which, after acidification, can be extracted with ether. The ether residue, heated with conc. sulphuric acid and a little resorcinol, yields fluorescein, which can be identified by its green fluorescent solution in alkali.



(ii) *Bromacetone* exhibits all the characteristic reactions of a ketone, yielding an oxime (m.p.  $36^{\circ}$  C.) and a crystalline bisulphite compound, and on mild oxidation gives a mixture of glycollic, formic, and acetic acids. It reacts violently with aqueous sodium sulphide, to give, on cooling, a precipitate of the corresponding sulphide.

(iii) *Ethyl iodo-acetate*, K.S.K.: The formation of iodide as a product of hydrolysis of a lachrymator may normally be taken as indicative of K.S.K. The other product of hydrolysis with alcoholic potash is the potassium salt of glycollic acid; which can be identified, after cooling and acidification with acetic acid, by adding a crystal of guaiacol and warming with a few drops of conc. sulphuric acid, when a violet colouration is produced.

(iv) *Bromobenzyl cyanide*, B.B.C.: gives a deep-red colouration with conc. sulphuric acid. On hydrolysis with cold alcoholic potash it forms potassium bromide and the dinitrile of diphenyl maleic acid. On boiling the reaction liquid the nitrile is hydrolysed, with evolution of ammonia, and after cooling and acidification with hydrochloric acid, a yellow precipitate of diphenyl maleic anhydride (m.p.  $156^{\circ}$  C.) is obtained.

(v) *Chloracetophenone*, C.A.P., which is used in warfare in the form of a non-persistent particulate cloud, stands in a different category from the other lachrymators, and it is improbable that any useful sample will normally be obtained. Chemically, C.A.P. is a relatively stable substance, unaffected by boiling water. The chlorine is, however, readily removed by hydrolysis with alkali (even warm sodium carbonate solution), and replaced by treatment with aqueous-alcoholic sodium thiosulphate, or warm aqueous sodium sulphide, yellowish-white needles of the corresponding sulphide (m.p.  $77^{\circ}$  C.) being obtained in the latter case. It gives an oxime (m.p.  $89^{\circ}$  C.), and a semicarbazone (m.p.  $156^{\circ}$  C.), and on oxidation with chromic acid yields benzoic acid.

(c) *Nose Irritants*.—As with C.A.P., it is very improbable that any useful samples of nose irritant gases will normally be obtained, physiological detection being, broadly speaking, the only practicable field method. Under favourable conditions, however, the presence of an arsenic-containing particulate on a filter can be established by (a) testing the filter for arsenic by the usual Kjeldahl-Gutzeit technique; (b) examining the behaviour of an alcoholic extract of the filter towards iodine in the presence of bicarbonate (decolorised by  $\text{As}^{111}$  compounds); or (c) igniting a filter paper moistened with a drop of the alcoholic extract, and noting the character of the irritation produced by the smoke.

In the unlikely event of sufficient sample being available for more detailed examination, its identity could, in general, be



established by carrying out an element test and a melting point determination, and if necessary confirmed by the preparation of its hydrolysis and oxidation products as under.

(i) *Diphenyl chlorarsine, D.A.*: Yields potassium chloride and the insoluble diphenyl arsenious oxide (m.p.  $92^{\circ}\text{C}.$ ) on hydrolysis with alkali. Oxidation with perhydrol, chloramine-T, or iodine in alcoholic solution in the presence of bicarbonate, gives the sparingly soluble diphenyl arsinic acid ( $\text{Ph}_2\text{AsO.OH}$ , m.p.  $175^{\circ}\text{C}.$ ). The chlorine atom is readily replaceable, the corresponding iodide (m.p.  $40^{\circ}\text{C}.$ ) being obtained on treatment with sodium iodide in acetone, and the sulphide (m.p.  $64^{\circ}\text{C}.$ ) on treatment with sodium sulphide in benzene, or hydrogen sulphide in alcohol.

(ii) *Diphenyl cyanarsine, D.C.*: Yields potassium cyanide and diphenyl arsenious oxide on hydrolysis with alkali, and diphenyl arsinic acid on oxidation as above.

(iii) *Diphenylamine chlorarsine, D.M.*: is distinguishable from D.A. and D.C. by its yellow-green colour (as solid). It dissolves to an intensely red solution in conc. sulphuric acid, and the solution gives the blue-green colour with nitric acid characteristic of diphenylamine, which is invariably present as an impurity in technical D.M. It is readily hydrolysed by alkalis to give the corresponding oxide (m.p.  $> 350^{\circ}\text{C}.$ ), and oxidised as above to phenarsazinic acid,  $\text{NH}(\text{C}_6\text{H}_4)_2\text{AsO.OH}$ , (needles, m.p.  $> 300^{\circ}\text{C}.$ ).

(d) *Vesicants*.—Vesicants of the dichlorarsine type (*e.g.* lewisite) will normally be detectable in the field from subjective indications (smell, irritant action, etc.). Mustard gas, however, gives no immediate physiological warning of its presence, and possesses no outstanding characteristic by means of which it can be rapidly recognised, apart from its rather weak and readily masked odour. A chemical test for the detection of mustard gas vapour has, therefore, been included in the G.I.O.'s portable testing and sampling equipment (*v.* Appendix I).

(i) *Mustard gas*: The presence of sulphur in a persistent war gas can normally be taken as indicative of mustard gas, and apart from direct element testing, can be readily established in the laboratory by destructive oxidation to sulphur dioxide, air containing the vapour being passed over powdered pumice in a red-hot tube, and the sulphur dioxide produced either detected as such by means of iodate-starch paper, or precipitated as sulphate by passing into a solution containing perhydrol and barium chloride.

The chlorine atoms of mustard gas are readily replaceable, *e.g.* by hydrolysis with alkali, or treatment with warm aqueous sodium sulphide solution, but few reactions of this type are suitable for identification purposes. The reaction with aqueous sodium iodide, to form the insoluble di-iodo derivative



(m.p.  $62^{\circ}\text{C}.$ ) is slow under ordinary conditions, but has been developed as a field test by the French chemist Grignard, by the incorporation of a small quantity of colloidal cuprous iodide as catalyst, and a little gum arabic as protective colloid. The Grignard reagent is not very sensitive, requiring  $0.025$  mgm. of mustard gas per c.c. to give an immediate turbidity, but is reasonably specific. Equally characteristic and more sensitive (capable of detecting  $0.01$  mgm. mustard gas), is the reaction with a 1 per cent. solution of  $\beta$ -naphthol in N/10 aqueous-alcoholic alkali, when the corresponding di  $\beta$ -naphthyl ether,  $\text{S}(\text{CH}_2\text{CH}_2\text{OC}_{10}\text{H}_7)_2$ , (m.p.  $133^{\circ}\text{C}.$ ); is slowly produced as a white turbidity (accelerated by warming).

As an organic sulphide mustard gas possesses reducing properties, and can accordingly be detected by the decolorisation of bromine water or permanganate solution, or by the reduction of selenium dioxide in hot sulphuric acid solution to an orange-red suspension of selenium. Such tests, however, though sensitive, are not in any way specific, similar reactions being also given by the trivalent arsenical gases and other reducing agents.

Oxidation of mustard gas with nitric acid or perhydrol in acetic acid yields the sulfoxide,  $(\text{ClCH}_2\text{CH}_2)_2\text{SO}$  (m.p.  $109-110^{\circ}\text{C}.$ ), and this on further oxidation with chromic acid gives the sulphone,  $(\text{ClCH}_2\text{CH}_2)_2\text{SO}_2$  (m.p.  $56-7^{\circ}\text{C}.$ ), both of which are somewhat soluble in water (1.2 and 0.6 per cent. respectively at  $20^{\circ}\text{C}.$ ). Oxidation with bleaching powder yields a variety of chlorinated oxidation products, and the reaction is violently exothermic, the mixture taking fire unless the bleaching powder is diluted with an inert material such as earth or water. The violence of this reaction can be used for identifying drops of liquid mustard gas, since no perceptible sign of reaction is given by other liquid war gases in contact with bleaching powder, with the exception of vesicants of the dichlor-arsine type, which react with evolution of fumes but much less violently than mustard gas.

The most characteristic tests for mustard gas are those depending on its reactions with heavy metal halides. When, for example, air containing mustard gas vapour is bubbled through a 0.1 per cent. aqueous solution of gold chloride, a yellow colloidal turbidity of insoluble addition product is formed when the amount of mustard gas exceeds about  $0.075$  mgm. per c.c. solution. Turbidities are also produced with potassium tri-iodide, iodo-mercurate, and iodo-bismuthate solutions. The iodoplatinate test incorporated in the G.I.O.'s equipment (Appendix I) depends essentially on reduction of the tetravalent platinum to the divalent condition, with concurrent liberation of elementary iodine. The mustard gas vapour is removed from the contaminated air by passage through glass wool moistened with 5 per cent. acetic acid solution, and on subsequent addition



of sodium iodo-platinate and of starch solution to the latter, a blue coloration develops if the amount of mustard gas present exceeds about 0.005 mgm. This test is reasonably specific: phosgene, diphosgene, chloropicrin, B.B.C. and K.S.K. vapours give no reaction, whilst the arsenical vesicants do not interfere unless present in exceptionally strong concentrations, when they tend to decolorise the reagent (sulphur dioxide has a similar decolorising effect). Chlorine and nitrous fumes give, of course, a positive reaction, and the test should therefore be applied by aspirating air *through* a contaminated ground sample, as described in Appendix I, in order to eliminate interference from such gases.

The destruction of mustard gas is most readily effected by hydrolysis (with boiling water, or alkali), or oxidation (with permanganate, conc. nitric acid, bleaching powder, chlorine, chloramine-T, etc.). Treatment with hot sodium sulphide or polysulphide solution is also effective, but it should be noted that the reaction between mustard gas and ammonia or its derivatives is too slow to be of practical value.

(ii) *Lewisite and other dichlorarsines*: The most characteristic reaction of lewisite is its instantaneous and quantitative decomposition on treatment with cold 15 per cent sodium hydroxide into acetylene, arsenite and chloride. Providing sufficient of the war gas is available (at least a small drop of the liquid), the liberated acetylene can be detected by means of ammoniacal cuprous chloride paper (red stain of copper acetylide), and the presence of arsenite and chloride in the solution established by the usual methods.

For the detection of lewisite vapour, its reaction with hydrogen sulphide may be used, though this is not specific, but applies to all alkyl dichlorarsines. When the vapour is collected in water, and a few drops of hydrogen sulphide water added, an opalescence or white precipitate of the corresponding sulphide,  $\text{RAsS}$ , is obtained if the amount of arsine present exceeds 0.02-0.05 mgm./c.c. solution. With lewisite excess of hydrogen sulphide is to be avoided as the precipitate (m.p.  $114^{\circ}\text{C.}$ ) redissolves.

Less sensitive than the hydrogen sulphide reaction, but of greater value for differentiating between lewisite and the other alkyl dichlorarsines, is their behaviour towards a solution of mercurous nitrate in water acidified with nitric acid. With lewisite a white precipitate is obtained: with ethyl dichlorarsine a white precipitate which turns grey owing to reduction to metallic mercury: whilst with methyl dichlorarsine an immediate grey precipitate is formed.

All the vesicants of the dichlorarsine type, including lewisite, are readily destroyed by oxidation with hydrogen peroxide, bleaching powder, etc., the corresponding arsonic acids,



$\text{R.AsO(OH)}_2$ , being formed. Treatment with alkali decomposes lewisite (*v.* above), and accelerates the hydrolysis of the alkyl dichlorarsines into the oxides,  $\text{RAsO}$ . The products in all cases are toxic and somewhat soluble in water.

(e) *Other Gases*.—Owing to their non-persistence, the paralyzants, hydrocyanic acid and hydrogen sulphide, and gases such as carbon monoxide and nitrous fumes which are likely to be encountered under war conditions as products of the incomplete combustion of explosives, can, in general, only be satisfactorily identified by means of tests carried out in the field, though in some cases useful indications may be obtainable from subsequent laboratory examination of vapour samples collected on charcoal. The reactions available for their detection and identification are detailed in most analytical text-books, and need not be referred to here. It is, however, relevant to point out that certain of these gases interfere with the iodoplatinate test for mustard gas vapour, and that the latter may therefore give misleading indications unless applied as directed in Appendix I, by aspirating air through a contaminated ground sample.

A similar procedure should be adopted when testing for mustard gas in a smoke-laden atmosphere. The question of the identification of smokes used for screening purposes will not normally arise, but can, if necessary, be effected by sampling through a particulate filter, and subsequently examining the latter by the usual analytical methods for the presence of phosphate, sulphate, tin, titanium, zinc, etc., and possibly also, arsenic, if the smoke was suspected of containing an arsenical nose irritant.

## (20) *General Laboratory Technique.*

(a) *Treatment of samples*.—Guided by subjective indications as to the general type of gas encountered, the samples collected by the G.I.O. may comprise

(i) air samples of non-persistent gases and particulate clouds, taken with a charcoal tube and cotton wool filter respectively, using the hand-pump;

(ii) samples of materials contaminated with persistent and semi-persistent gases—earth, plaster, drops absorbed on filter paper, etc.

In the subsequent chemical examination of such samples to establish or confirm the identity of the gas present, the following general procedure should be adopted.

(i) *Non-persistent gases and particulate clouds*.—Samples will not normally be obtainable, but if taken, the examination should be on the following lines:

(a) *Filter*: Either examine as a whole for arsenic; or if a reasonable amount of particulate matter has been



collected, extract with hot alcohol, evaporate the extract on a water-bath, and examine the residue for elements, m.p., etc. A rapid differentiation between C.A.P. and nose irritants in general can be effected by examining the behaviour of the extract towards iodine-starch solution in the presence of sodium bicarbonate (decolorised by As<sup>111</sup> compounds), or alternatively by igniting a filter paper moistened with a drop of the extract, and noting the character of the irritation produced by the smoke.

(b) *Charcoal*: Test a few of the charcoal granules for elements etc., by the method of Dijkstra (Chem. Weekblad, 1937, **34**, 351). Warm remainder with alcoholic potash, filter, and examine the solution for halides, nitrite, and other products of hydrolysis.

(ii) *Persistent and semi-persistent gases*.—The sample bottles should be opened in a well-ventilated fume-cupboard and examination effected as under:

(a) *Persistent lachrymators*: If the gas present appears from subjective indications to be a persistent lachrymator, extract a portion of the sample with alcohol, add alcoholic potash to the filtered extract, hydrolyse by warming gently, and examine the products as under Sect. (19) (b).

(b) *Other gases*: If the presence of other gases is indicated or suspected, replace the screw-cap of the sample bottle by a rubber bung carrying two glass tubes, and aspirate air over the sample. As a "sorting" test, pass the effluent air stream through alcoholic potash, and test portions of the latter, after acidification, for (1) halides and cyanide (precipitate with silver nitrate): (2) nitrite (red colour with Griess-Ilosvay reagent): and (3) arsenite (production of arsine on reduction with zinc). Confirm the preliminary indications by testing the effluent air successively with reagents characteristic of the various gases: *e.g.*, for diphosgene apply the aniline reaction: for mustard gas, the iodoplatinate or gold chloride reactions: and for lewisite and other dichlorarsines, the hydrogen sulphide and mercurous nitrate reactions.

(Important note: When using bubblers containing liquid reagents, only one such bubbler should be inserted in the air stream at a time. The simultaneous use of several bubblers in series is fundamentally unsound.)

(b) *Air-flow analysis*.—Air-flow analysis, as described in (ii) (b) above, will in general be the simplest, safest, and most satisfactory method of examining samples of contaminated materials, and should be adopted whenever practicable.



With this method, using reaction bubblers of simple type, the air should be aspirated relatively slowly (up to *ca.* 500 c.c./min.), and if the sample is only lightly contaminated, better results will be obtained by surrounding the bottle containing the sample with hot water. The ingoing air should preferably be purified by passing through a charcoal tube, and dried with calcium chloride; and as far as possible, all joints should be glass-to-glass to avoid absorption by the rubber connecting tubes of gases such as phosgene, chloropicrin, and mustard gas, which are highly soluble in rubber.

Within limits, the sensitivity of the reactions employed can be artificially increased, and the time taken to examine a lightly contaminated sample correspondingly reduced, by modification of technique so as to effect rapid contact between the maximum amount of war gas vapour and the minimum amount of reagent solution: *e.g.*, by the use of higher rates of flow in conjunction with special types of bubblers in which the ingoing air-stream is broken up to a greater or lesser extent; or alternatively and more simply, by passing the air over a suspended drop of the reagent.

Under standardised conditions, a rough indication of the degree of contamination of the sample under examination is, of course, obtainable from the intensity of the reaction produced.

(c) *Extraction methods.*—An alternative procedure for dealing with samples which are obviously grossly contaminated with liquid gas, is to extract them with anhydrous ether, free the extract from ether by spontaneous evaporation in a gentle air flow in a well-ventilated fume-cupboard, and examine the reactions, etc., of the residue. Provided that at least several drops of residue are available, a determination of its boiling point, a sodium fusion to determine the elements present, and an examination of its behaviour to water and alkalis, can be made, and will naturally help considerably towards its identification.

Analytical schemes on this basis, such as that proposed by Studinger (*v.* translation in *Chem. and Ind.*, 1937, **56**, 225), must, however, be applied with reservation, as such preliminary tests may give misleading results if, as is probable, the war gases are present in admixture, or in solution in an organic solvent containing chlorine, etc. The ether extraction procedure is, moreover, somewhat dangerous, necessitating the wearing of a respirator, and involving the risk of fire and explosion (the latter particularly with chloropicrin), and has, in general, little to recommend it over air-flow analysis so far as concerns identification of the majority of the well-known war gases.



Extraction methods may be necessary in dealing with samples contaminated with persistent lachrymators, but in such cases alcohol is usually preferable to ether as a solvent, as the subsequent hydrolysis is effected in that medium.

In this connection, also, it should be borne in mind that solvent extracts of samples contaminated with mustard gas may contain thiodiglycol, its innocuous hydrolysis product. The latter gives the same iodoplatinate reaction as unhydrolysed mustard gas, and it is therefore necessary to employ the less sensitive but more specific  $\beta$ -naphthol or gold chloride tests to enable a differentiation to be made between the two. This difficulty does not arise with the air-flow method, since thiodiglycol is virtually non-volatile.

(d) *Examination of contaminated foodstuffs and water.*—The examination of foodstuffs and water suspected of having been contaminated with war gases will not be the responsibility of G.I.O.'s, though they may be called upon to advise and report when such contamination has occurred.

So far as concerns foodstuffs, where these have been exposed to vapour only, it will, in many cases, be possible to render them safe for consumption, though possibly still somewhat unpalatable, by airing for a day or so: where, however, liquid contamination has occurred, removal and destruction of at least the outer layers of the contaminated material will be necessary. In either case, of course, the treatment would have to be continued until the materials gave completely negative results on subsequent chemical and physiological examination.

As regards the contamination of water supplies by war gases, filtration through an ordinary filter-bed will remove all undissolved gas and insoluble products of hydrolysis, and the amount of dissolved gas and/or toxic decomposition products present in the filtered water will, in general, only be significant in the case of small reservoirs which have been heavily contaminated with liquid gas. Where mustard gas is the contaminant, any gas dissolved in the filtered water will be slowly destroyed by hydrolysis, and after standing for 24 hours (or on a small scale boiling for 15 minutes) the water, though possibly unpalatable, can be safely used for drinking purposes. With lewisite and other arsenical gases, however, special chemical treatment will be necessary to remove dissolved toxic products from the water.

(e) *Testing for freedom from contamination.*—The question of testing areas and objects for freedom from gas will normally only arise in the case of contamination by vesicants, and mustard gas in particular, since it will usually be evident from subjective indications whether other types of gases are still present in significant quantities.



Areas which have been contaminated with mustard gas may be considered as safe for traversing if the surface layers show no sign of the presence of liquid gas when tested in the usual way by means of detector paper (*cf.* Sect. (13) (b)). Where, however, occupation of a decontaminated area is concerned, representative portions of the decontaminated surface should be tested chemically, by sampling the air in their immediate vicinity and applying the iodoplatinate test. If the surface is loose, the best results will be obtained by aspirating air *through* a sample of the decontaminated material (*v.* Appendix I), but where this is impracticable, the sampling should be effected through an inverted sampling funnel placed close to the decontaminated surface. The surfaces selected for test should be comparatively dry, and as free from bleaching powder as possible, to avoid possible interference from hypochlorous acid. Under these conditions a negative result with a 40 pump-stroke sample may be taken as indicating that no vapour danger would arise from ordinary occupation of the area in question, though the possibility of skin effects resulting from prolonged intimate contact with the "decontaminated" surface is not excluded.

Decontaminated objects in general may similarly be considered safe for handling if they give negative results when tested in the same way. In the case of articles which may come into intimate contact with the body for appreciable periods, the preliminary chemical examination should be supplemented physiologically, by actual skin-contact tests, before they are accepted as safe for use.

(f) *Decontamination of apparatus.*—All apparatus employed in the examination of contaminated materials will require some form of decontamination treatment after use, in order to destroy all traces of war gas.

For the destruction of most gases treatment with hot alcoholic potash is suitable, but in certain cases other reagents are more convenient. Washing in running water alone, for example, rapidly destroys diphosgene; cold aqueous alkali decomposes lewisite; and a hot aqueous-alcoholic solution of sodium sulphite is useful for destroying chloropicrin. As regards mustard gas, treatment with conc. nitric acid is the most convenient laboratory method for decontaminating glassware, whilst rubber connecting tubes, metal forceps, and similar articles are best treated by immersion in boiling water for 30 minutes.

Similar remarks apply to the G.I.O.'s portable sampling and testing equipment, all parts of which, contents and case, need to be adequately decontaminated after use in a gas-contaminated area (*v.* Appendix I).

This thorough decontamination is essential, not only from the point of view of personal safety, but also to avoid introducing uncertainties into subsequent work due to the presence of small residual traces of gas in the apparatus.



TABLE I.—PHYSICAL PROPERTIES OF THE WAR GASES.

War Gas.	Mol. Wt.	Freezing Point.	Boiling Point.	Density	Vapour Density.	Vapour Pressure.	"Volatility."	"Persistence."*
		°C.	°C/760mm.	D <sup>20</sup> <sub>4</sub> (gms./c.c.).	N.T.P. (air = 1).	20° C. (mm. Hg.)	= Saturation conc. (mgm/l) at 20° C.	At 20° C. (approx. relative time for evaporation, Water = 1).
<i>Lung Irritants—</i>								
Chlorine ...	70.9	-102	-33.6	(1.41)	2.5	5031	gas	N.P. gas
Phosgene ...	98.9	-118	+ 8.2	(1.38)	3.5	1173	gas	N.P. gas
Diphosgene ...	197.9	- 57	128	1.65	6.9	10.3	112	0.38
Chloropicrin ...	164.5	- 69	112	1.66	5.7	18.3	165	0.23
<i>Lachrymators—</i>								
Xylol bromide	185	—	210—220	1.4	6.4	0.07	0.7	58
Bromacetone	137	- 54	136	1.63	4.7	9	68	0.5
K.S.K. ...	214	- 21	179	1.8	7.4	0.54	6.3	6.9
B.B.C. ...	196	+ 25.4	242 (dec.)	1.52	6.8	0.012	0.13	325
C.A.P. ...	154.5	+ 58	244	1.32	5.3	0.013	0.105	N.P. Cloud
<i>Nose Irritants—</i>								
D.A. ...	264.5	+ 38	333	1.4	—	0.0005	—	N.P. Cloud
D.C. ...	255	+ 33	377 (calc)	1.45	—	0.0002	—	N.P. Cloud
D.M. ...	277.5	+195	410 (calc)	1.65	—	2 × 10—13	—	N.P. Cloud
<i>Vesicants—</i>								
Mustard Gas	159	+ 14.4	217 (dec.)	1.28	5.4	0.11	0.96	38
Lewisite I	207.3	- 5	190 (dec.)	1.89	7.2	0.4	4.5	9.5
Me. dichlorarsine ...	161	- 42.5	133	1.84	5.5	8.5	75	0.5
Et. dichlorarsine ...	175	< 65	155	1.66	6.0	2.3	22	1.8
<i>Paralysant—</i>								
Hydrocyanic acid ...	27	- 15	26.5	0.7	0.94	610	901	0.02

\* As a rough guide the unit of the quoted persistence values may be taken as approximately one hour in dry weather on open even ground.



TABLE II.—ODOUR AND IRRITANT EFFECTS OF THE WAR GASES.

War Gas.	Odour.		Irritant Effects.		Intolerable Concentration.	Haber's "Tödlichkeits Produkt."
	Character.	Minimum perceptible concentration (mgm./cu. m.).	Nature.	Threshold of Action (mgm./cu. m.).		
<i>Lung Irritants—</i>						
Chlorine ...	Pungent ...	10—15	Throat irritation	45	150—200	7,500
Phosgene ...	Musty hay, suffocating.	5—10	Throat irritation	10—15	40	450
Diphosgene	Like phosgene, but more unpleasant.	5—10	Throat irritation	5—10	40	500
Chloropicrin	Sweetish, penetrating	8	{ Lachrymation Throat irritation	15—20 75	50—100	2,000
<i>Lachrymators—</i>						
Xylol bromide	Pungent, aromatic; like elder leaves in dilution.	0.3	Lachrymation	1.8	15	6,000
Bromacetone	Pungent, stifling	0.5	{ Lachrymation (Skin Irritant as liquid)	1.5	10	4,000
K.S.K.	Pear drops	< 1	Lachrymation	1.4	15	1,500
B.B.C.	Sour fruit, burning	Irritates before odour is perceived.	Lachrymation	0.2	30	7,500



C.A.P.	...	Aromatic, apple blossom.	0.2	{ Lachrymation Skin irritation	0.3 2	4.5	4,000
<i>Nose Irritants—</i>	...						
D.A.	...	Aromatic, irritant	0.3	{ Nose and throat irritation.	0.1	1-2	4,000
D.C.	...	Bitter almonds, irritant.	0.01		0.05-0.1	0.25	4,000
D.M.	...	Practically odourless	—		0.1	0.4	—
<i>Vesicants—</i>							
Mustard Gas	...	{ Pure: faint, leek-like. Crude: garlic, mustard, horse-radish, etc.	ca 1 0.3 or less	{ No immediate irritant effects	—	—	1,500
Lewisite	...	{ Pure: almost odourless, irritant. Crude: geraniums, intolerable.	14 < 1	{ Nose and throat irritation.	1	Low, but no definite value available.	1,500
Me. dichlorarsine	...	Fruity, irritant	0.5-1	{ Nose and throat irritation.	2	25	3,000
Et. dichlorarsine	...	Fruity, irritant	0.8		1.5	10	3,000
<i>Paralysant—</i>							
Hydrocyanic acid	...	Bitter almonds	1	None	—	—	1,000-4,000



TABLE III.—CHEMICAL PROPERTIES OF THE WAR GASES.

War Gas.	Behaviour to water.	Products of Hydrolysis.		Neutralising Agents.
		With Water.	With Alkali.	
<i>Lung Irritants</i> —				
Chlorine ...	Somewhat soluble ...	HCl and HOCl ...	As with water ...	Alkali, etc. Alkali; alkaline phenates; amines (particularly hex-amine). Alcoholic potash; alkali polysulphide; aqueous-alcoholic sodium sulphite.
Phosgene ...	Rapidly hydrolysed	HCl and CO <sub>2</sub> ...	As with water ...	
Diphosgene ...	Stable ...	—	With KOEt gives KCl, KNO <sub>2</sub> , and C(OEt) <sub>4</sub> .	
Chloropicrin ...	Stable ...	—	—	
<i>Lachrymators</i> —				
Xylol bromide ...	Slowly decomposed	As with alkali ...	KBr, and Me. C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH ...	Alkali.
Bromacetone ...	Stable ...	—	KBr, and Me. COCH <sub>2</sub> OH ...	Alkali; sodium thiosulphate.
K.S.K. ...	Stable ...	—	KI and CH <sub>2</sub> OH. COOK ...	Alkali; sodium thiosulphate.
B.B.C. ...	Stable ...	—	With Alc. KOH gives KBr and (PhC(CN)=) <sub>2</sub> .	Alcoholic alkali.
C.A.P. ...	Stable ...	—	KCl and PhCOCH <sub>2</sub> OH ...	Alkali; sodium thiosulphate.
<i>Nose Irritants</i> —				
D.A. ...	Slowly hydrolysed	As with alkali ...	KCl and (Ph <sub>2</sub> As) <sub>2</sub> O (toxic) ...	Alkali; chlorine; oxidising agents (peroxide; chlorine-T; Iodine in presence of sodium bicarbonate).
D.C. ...	Stable ...	—	KCN and (Ph <sub>2</sub> As) <sub>2</sub> O (toxic) ...	
D.M. ...	Stable ...	—	KCl and corresponding oxide (toxic).	



<i>Vesicants</i> — Mustard Gas	...	Slowly hydrolysed (rapidly on boiling).	HCl and thiodiglycol (non-toxic).	As with water. (With conc. alc. KOH gives foul smell- ing vapours of divinyl sul- phide).	Oxidising agents (permangan- ate, nitric acid, etc). Chlorine; bleaching powder; chloramine-T; Aqueous sodium sulphide (slow).
Lewisite ...	...	Rapidly hydrolysed	HCl and $\text{ClC}_2\text{H}_2\text{AsO}$ (toxic, sparingly soluble).	Decomposed into $\text{C}_2\text{H}_2$ , KCl, and $\text{K}_3\text{AsO}_3$ .	Alkali; bleaching powder; hydrogen peroxide.
Me. dichlorarsine Et. dichlorarsine	}	Rapidly hydrolysed	HCl and the corres- ponding oxide, $\text{RAsO}$ (toxic; sol- uble).	As with water	Alkali; oxidising agents.
<i>Paralysant</i> — Hydrocyanic acid		Miscible: slowly de- composed.	Ammonium formate, and brown poly- meric products.	KCN (toxic)	Alkali.



## APPENDIX I

## THE G.I.O.'s. SAMPLING AND TESTING EQUIPMENT.

(1) *Nature of Equipment.*

The portable Sampling and Testing Equipment to be supplied for use of G.I.O.'s. consists essentially of a partitioned metal case, approximately 9 in. by 4½ in. by 4½ in., supported by means of a webbing belt, and carrying on its hinged lid a detachable metal suction pump with screwed-in, right-angled adaptor.

The contents of the case comprise:—

## (a) Apparatus for sampling contaminated materials:—

- (i) Three wide-mouth 4 oz. glass bottles, with bakelite screw caps, numbered 1, 2, 3.
- (ii) A dozen small wooden spatulae.

## (b) Apparatus for testing for mustard gas:—

- (i) Six cloth-diaphragmed sampling funnels, to fit over the pump adaptor.
- (ii) Ten sampling-tubes containing glass wool moistened with dilute acetic acid, and fitted with red rubber rings, for insertion in the pump adaptor.
- (iii) A dropping-tube containing iodoplatinate solution (Reagent A).
- (iv) A dropping-tube containing starch solution (Reagent B).

## (c) Miscellaneous:—

- (i) Two sampling-tubes as (b) (ii), but with black rubber rings, and containing activated charcoal between plugs of cotton wool. (For general vapour and particulate sampling).
- (ii) A supply of detector paper. (For assisting in the delineation of contaminated areas.)
- (iii) Sundries, such as forceps, filter paper, cotton wool, etc. (For mopping up liquid drops.)

In addition to this case, a partitioned canvas haversack is also provided, to contain:—

## (i) In the compartment nearest the wearer:—

A note book, a number of report forms (*v.* Appendix II), pencil and torch.

## (ii) In the central compartment:—

Three metal canisters lined with corrugated strawboard, for the reception of filled sample bottles; and the G.I.O.'s. rubber manipulative gloves. (A reserve supply of sampling funnels and spatulae may be carried if necessary.)

## (iii) In the outer uncovered compartment:—

A pair of oilskin anti-gas gloves.

## (iv) In the small side-pocket:—

Used sampling tubes.

Both items of equipment are normally carried by the G.I.O., the metal case being worn on the left side of the belt, and the haversack attached by spring hooks to the right side of the same belt. The equipment should, of course, be put on over the anti-gas clothing, and after the respirator has been adjusted in the alert position.



(2) *Method of use.*

To avoid unnecessary contamination of the interior of the sampling case, the detailed instructions given below should be strictly followed. It is assumed that the G.I.O. has made his preliminary reconnaissance, and is standing, with his assistant, up-wind of the contaminated area. He will, normally, be wearing the rubber manipulative gloves provided for his use, and must put on his respirator, if not already adjusted, before commencing operations.

(a) *Testing for mustard gas.*—The G.I.O. first detaches the pump, and holds it with adaptor uppermost in his left hand. With his other hand he opens the case, inserts a sampling-tube into, and a sampling funnel over, the pump adaptor, removes a sampling spatula (*v. Note (1)* below), and closes the case. Holding both pump and spatula in his left hand, he then slips an oilskin anti-gas glove over the rubber glove on his right hand (with assistance if available, *v. Note (2)*), transfers the spatula to this hand, and walks to the edge of the heavily contaminated area, selecting as far as possible a part of the latter where the surface material is loose enough to be dug out with the spatula (*v. Note (1)*).

Using the latter he partially fills the sampling funnel with contaminated material, lays the spatula on the ground (*v. Note (3)*), and aspirates 40 pump-strokes of air through the sample, still holding the pump in his left hand, and working it with his doubly-gloved right hand. Subsequently he removes the filled sampling funnel from the end of the adaptor, places it on the ground (*v. Note (3)*), and walks back to his original position up-wind of the contaminated area (*v. Note (4)*).

There, he slips the outer glove off his right hand (*v. Note (2)*), opens the metal case with this hand, and by means of the dropping-tubes, transfers two drops of Reagent A, followed by two drops of Reagent B, to the sampling-tube in the adaptor. Finally, he takes the sampling-tube out of the adaptor, still using his right hand, gives it one sharp shake, and inspects the colour of the contents. The latter will be blue if mustard gas is present, but rose-red in the absence of gas (*v. Note (5)*).

Subsequently the G.I.O. places the used sampling-tube in the small side-pocket of the haversack, closes the metal case, and replaces the pump on the lid of the case.

If the test gives conclusive results the G.I.O. should immediately make his report on one of the forms provided (*v. Appendix II*), but if still uncertain of the nature of the gas he should take a sample of contaminated material for subsequent examination, adopting the procedure detailed below.

(b) *Sampling contaminated materials.*—The G.I.O. opens the sampling case, takes out a sample bottle and a wooden spatula (if required, *v. Note (1)* and *(3)*), and recloses the case. He unscrews the bakelite cap from the bottle, and hands it to his assistant to hold (or, if working alone, places it in the central compartment of the haversack). Holding both bottle and spatula in his left hand, he then slips on oilskin anti-gas glove over the rubber glove on his right hand (*v. Note (2)*), transfers the spatula to this hand, and walks to the edge of the heavily contaminated area, selecting as in (a) a portion of the latter where the surface material is loose enough to be dug out with the spatula (*v. Note (1)*).

Using the latter he fills the sample bottle with grossly contaminated material, taking care not to contaminate the outside of the bottle, lays the spatula on the ground, and walks back to his original position up-wind of the contaminated area (*v. Note (4)*). He then slips the outer glove off his right hand (*v. Note (2)*), and with this hand takes the bakelite cap from his assistant (or, if working alone, recovers it from the central compartment of the haversack), and screws it firmly in position over the mouth of the bottle.



Subsequently the closed bottle is inserted in one of the metal canisters provided for the purpose, the lid of the latter is put on, and the whole placed in the central compartment of the haversack. The number of the bottle containing the sample should be noted by the G.I.O. on his report form, and the sample itself subsequently disposed of as indicated in Section (3) below.

No special precautions or instructions are necessary regarding general vapour and particulate sampling, to effect which, one of the charcoal-filled sampling-tubes is inserted in the adaptor, and as much of the contaminated air as possible is aspirated through it by means of the pump. The case should be kept closed during the actual sampling, but the used tube may be afterwards re-inserted in it, the number of the tube being, of course, duly noted on the appropriate report form.

(1) *Notes on Testing and Sampling.*—The wooden sampling spatulae will be of greatest service where the surface material of the contaminated area is comparatively loose, and can be dug out or scraped off. With very hard surfaces, or where liquid gas is visible as droplets on metal-work, painted wood-work, foliage, etc., it may be preferable to absorb superficial liquid contamination on swabs of cotton wool or strips of filter paper, and place these in the sampling funnel or sample bottle. The precise nature of the sampling equipment to be removed from the case will, therefore, depend to some extent on circumstances: a decision on this point should, however, be made before starting the actual sampling operations, for under no circumstances should the sampling case be opened whilst the G.I.O. is in the heavily contaminated zone.

(2) Under normal conditions of working, the oilskin anti-gas glove will be put on and taken off with assistance from the G.I.O.'s assistant. Where, however, assistance is not available, the G.I.O. will have to accomplish this alone, using the outer compartment of the haversack as a grip for the loose glove.

(3) When testing for mustard gas, the used spatula and sampling funnel should be placed on the ground at the edge of the heavily contaminated zone, and not thrown away into the middle of the latter. If the test gives inconclusive results it will be necessary to take away a sample of the contaminated material, in which case the spatula already employed will, naturally, be re-used, and the procedure detailed in (b) above will be modified accordingly. In certain cases, also, particularly where the quantity of removable contaminated material is limited, it may be advantageous to take away for subsequent examination the actual sample tested on the spot.

(4) The G.I.O. should be particularly careful not to let any part of his clothing or equipment come into contact with the contaminated material unnecessarily during the sampling operations; and when returning up-wind of the contaminated area, he should wipe his boots, doormat fashion, in dust or other absorbent material, to avoid spreading the contamination (v. Section (16) (d)).

(5) The intensity of the blue colouration produced will depend on the degree of contamination of the material under examination. The test should always be carried out as described, i.e. by aspirating air through a sample of contaminated material, so as to eliminate interference from gases such as chlorine and nitrous fumes which also give a positive reaction with the reagents (v. Section (19) (d)). If the contents of the tube appear pale yellow after addition of reagents A and B, the presence of lewisite or other dichlorarsine in the sample should be suspected.

### (3) *Decontamination and refitting.*

After a tour of duty in which blister gas has, or may have, been encountered, the G.I.O. and his assistant, in common with other A.R.P. personnel, will proceed to a depot for cleansing and decontamination.



At this station, as a routine measure, the G.I.O.'s portable sampling and testing equipment will be subjected to a preliminary decontamination treatment, comprising:

(a) decontamination by solvent swabbing of the exterior of the metal sampling case, the outsides of the metal canisters in the haversack, and the exterior of the torch.

(b) decontamination by airing (if only contaminated by vapour) or destruction by burning (if contaminated by liquid) of unused report forms, pencil, etc.

(c) decontamination by immersion in boiling water of the webbing belt and canvas haversack, and of the rubber manipulative and oilskin anti-gas gloves (together with the rest of the anti-gas clothing and equipment worn by the G.I.O. and his assistant).

The used sampling tubes in the side pocket of the haversack will be transferred to a metal container provided for the purpose, and this, together with the decontaminated sampling case and metal canisters will be returned immediately to the G.I.O., who will subsequently prepare for despatch to the Senior Gas Adviser any samples taken for examination, and systematically decontaminate and refit the interior and contents of the sampling case. Facilities for carrying out such work will be provided at the depot.

With regard to the preparation of samples for despatch, if the procedure described in Sect. (2) (b) has been followed, these will already be contained in closed sample bottles which have themselves been placed in the metal canisters provided for the purpose. The free space in the top of the latter should be filled with charcoal or other absorbent material, the lid of the canister firmly secured in position by means of adhesive tape, and the whole adequately parcelled up and labelled. In the unlikely event of a general vapour or particulate sample having been taken, the charcoal tube concerned should be packed in cotton wool in a small wood or metal box.

The used sampling tubes in the metal container should be emptied of their contents, using forceps decontaminated by immersion for a few minutes in boiling water, and after drying, re-filled as described below. The container itself should be rinsed out with several changes of water and allowed to dry. It should be reserved solely for the reception of used sampling-tubes.

Decontamination of used sample bottles will not, in general, be the responsibility of the G.I.O. If occasion arises, however, the residual contents should be carefully transferred to a hole in the ground and buried, and the bottle and screw cap subsequently decontaminated in the usual way by immersion for 30 minutes in boiling water. The waxed disc in the screw cap will need replacement before the bottle is re-used. The metal canisters containing the sample bottles can similarly be decontaminated by immersion in boiling water, and after drying, re-lined with corrugated strawboard.

As regards decontamination of the contents of the sampling case, these will normally only have been exposed to vapour, and airing for an hour or so will be sufficient to remove any trace of gas remaining. If, however, the interior of the case is suspected of having been contaminated with liquid gas, the whole should be dismantled and systematically decontaminated, the glassware and rubber articles being immersed in boiling water for 30 minutes, and the metal parts swabbed with solvent and aired. The absorbents contained in the unused sampling-tubes should in this case be replaced, but the reagents, being in closed dropping tubes, can normally be regarded as unaffected: the stoppers of the latter, however,



should be removed and decontaminated by boiling, and the outsides of the tubes themselves cleaned by solvent swabbing. The test papers, cotton wool, wood sampling spatulae, and so on, if contaminated with liquid gas, will have to be destroyed by burning and replaced. (This procedure applies primarily to contamination by liquid mustard gas or lewisite. If the contaminant is a persistent gas of another type, it may be necessary to employ a method of decontamination other than immersion in boiling water, such as, e.g., treatment with alcoholic alkali: v. Sect. (20) (f).)

Finally, the decontaminated apparatus should be re-assembled and re-fitted as necessary to conform with the list of contents given in Sect. (1) of this Appendix. The subjoined instructions should be followed in preparing the sampling-tubes, etc., for use.

(a) Sampling-tubes for mustard gas tests: Insert a lightly packed wad (approx. 0.1 gm.) of glass wool into each tube, moisten with a few drops (*ca.* 0.25 c.c.) of 5 per cent. acetic acid solution, allow to drain for some minutes, and remove with filter paper any liquid in the tip of the tube before placing the latter in the case. The acetic acid solution should be made up by adding 5 c.c. of A.R. glacial acetic acid, free from reducing impurities, to 95 c.c. of distilled water and stirring well.

(b) Sampling tubes for general vapour, etc., sampling: Insert a plug of cotton wool into the tubes, followed by about 0.2 gm. of 7-18 B.S.S. mesh activated nut-shell charcoal, and finally a second plug of cotton wool, pressing the latter firmly into position.

(c) Dropping tubes for reagents: The dropping tubes should not be filled more than about half full (*ca.* 5 c.c.).

(i) Reagent A: The iodoplatinate reagent keeps indefinitely in closed bottles, and should be used as supplied.

(ii) Reagent B: The starch solution should be made up freshly every few days, by rubbing 0.1 gm. of "soluble" starch to a cream with a little water, and adding to 10 c.c. of boiling water.

Supplies of the necessary solutions, etc., and of expendable items such as sampling funnels, wooden spatulae, etc., will be held at all centres where re-fitting is to be carried out. Local arrangements will also be made for the replacement of used sample bottles and metal canisters, etc., and for the re-issue of decontaminated webbing belts, canvas haversacks, and so on.

Under active service conditions an individual issue of the portable sampling and testing equipment will be made to each G.I.O., who will be personally responsible for maintaining it in a condition of readiness.



## APPENDIX II

## REPORT FORM FOR USE OF GAS IDENTIFICATION OFFICERS.

Serial No.....

CENTRE.....

Report from G.I.O. No.....

Date..... Time.....

POSITION OF GAS BOMB : .....  
.....

TYPE OF GAS : (Delete items not applicable, and record nature of gas if identified).

Non-persistent : Lung Irritant.....

Toxic Smoke.....

Persistent : Lachrymator.....

Vesicant.....

## DANGER AREAS :

Liquid Contamination.....  
.....Vapour or Gas Cloud.....  
.....OTHER PARTICULARS (if any) .....  
.....

Signature.....

IF GAS NOT IDENTIFIABLE give particulars below :

General characteristics:.....  
(Appearance, smell,  
etc.) .....Any physiological effects observed : .....  
.....  
.....Samples taken : .....  
(Quote tube or bottle .....  
No.) .....











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